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Trihalomethane Precursor Removal by Coagulation Techniques in a Lime-Softening Plant (A Three-Phased Study)

Daytona Beach, FL

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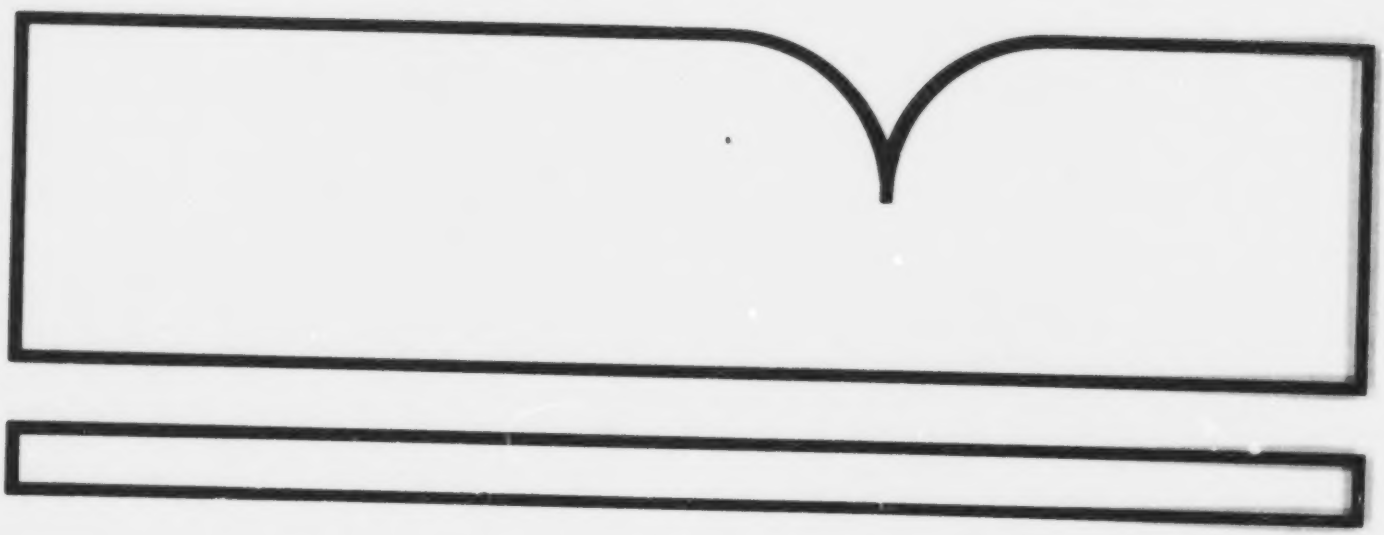

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TRIHALOMETHANE PRECURSOR REMOVAL BY COAGULATION TECHNIQUES IN A LIME-SOFTENING PLANT (A Three-Phased Study)

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16. ABSTRACT

A research program identified and evaluated a treatment scheme that reduced trihalomethane (THM) concentrations formed in the treatment process by coagulating the THM precursor materials and removing them before chlorination. The process was evaluated in bench testing in an 18.9 L/min pilot plant and in a plant-scale trial that simultaneously compared the potential for precursor removal from a Florida ground water by conventional lime softening and by lime softening with a new polymeric coagulant (XE-392, Rohm and Haas). The correlation of total organic carbon (TOC) and ultraviolet (UV) absorbance with total trihalomethanes was investigated in an effort to establish an easily performed process control test. In general, reductions in trihalomethane formation potential concentrations were less than UV absorbance reductions but greater than TOC concentration reductions. No secondary deterioration in water quality was noted from the experimental treatment scheme and no major operational problems were experienced during the trial. The experimental coagulant system reduced THM concentrations by more than 50 percent compared to the conventional treatment methods used in the Daytona Beach treatment plant. A cost estimate was prepared. If the experimental coagulation process is used, the water treatment plant operating costs would climb from 33¢/1000 gallons to 75¢/1000 gallons. These projected costs are considered too high to warrant the use of this polymeric coagulant in Daytona Beach, Florida.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report describes a study conducted in Daytona Beach, Florida, that evaluated improved coagulation techniques in a lime softening process using an experimental polymeric coagulant. The effects of these techniques in reducing trihalomethane formation potential in a ground water supply were investigated in both pilot- and plant-scale trials.

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Water Engineering Research
Laboratory

PREFACE

In 1979, the U. S. Environmental Protection Agency promulgated an amendment to the National Interim Primary Drinking Water Regulations establishing a maximum contaminant level (MCL) of 0.10 mg/L for total trihalomethanes (THMs). Previous investigations conducted at the Ralph F. Brennan Municipal Water Treatment Plant in Daytona Beach, Florida, indicated that the level of THMs in the finished water was several times greater than the MCL.

These studies further concluded that the level of THM production could be reduced by improving coagulation and by altering the point of chlorination in the treatment process. Treatment modifications would not, however, reduce effluent THM concentrations below the MCL. The precursor compounds naturally present in the raw well water source used by Daytona Beach were reported to be especially resistant to removal through conventional lime softening and coagulation techniques.

During an EPA-sponsored pilot plant investigation conducted in 1981, an experimental polymeric coagulant (XE-392, Rohm & Haas) showed promise for removing organic precursor materials. This research program was subsequently undertaken to:

1. Develop a lime softening process using the experimental polymeric coagulant, which by itself or in conjunction with additional coagulants would result in compliance with the established MCL for THMs.

2. Use a full-scale plant trial to investigate process performance, effects of the process on the operability of the various treatment system unit operations, methods of process control, and treatment costs.

The research program was conducted in three phases: Evaluation of the process in bench-scale experiments, pilot-plant testing, and a plant-scale trial. The pilot plant used was the EPA trailer-mounted coagulation, clarification, and filtration system loaned to the City of Daytona Beach. Plant-scale testing was conducted at the Ralph F. Brennan Water Plant, where a flow of 0.13 m^3/s (3 mgd) was treated for 30 days.

ABSTRACT

A research program identified and evaluated a treatment scheme that reduced trihalomethanes (THMs) formed in the treatment process by coagulating the THM precursor materials and removing them before chlorination. The process was evaluated in bench testing in an 18.9-Lpm pilot plant and in a plant-scale trial that simultaneously compared the potential for precursor removal from a Florida groundwater by conventional lime softening and by lime softening with a new polymeric coagulant (XE-392, Rohm & Haas).

The study was conducted at a Daytona Beach water system composed of two lime softening plants. The system normally produces a finished water with average THM concentrations of 100 µg/L at the plant and more than 200 µg/L in the distribution system. Current treatment processes include lime softening, coagulation, fluoridation, chlorination to a free residual, and mixed media filtration.

Previous studies of this system were directed toward reducing THM concentrations through change in point of chlorination and improvements in the coagulation process. In a 1981 pilot plant investigation, an experimental polymeric coagulant showed promise for removing organic THM precursor materials.

The current research program evaluated the use of the experimental product, XE-392, by itself and in conjunction with conventional coagulants. Bench scale tests screened a number of coagulant combinations. The most promising treatment scheme was then evaluated in an 18.9-Lpm (5-gpm) trailer-mounted pilot plant.

Following successful pilot plant operation using XE-392, ferric sulfate, and a nonionic polymer in a lime softening process, the same treatment scheme was evaluated on a full-scale basis. A flow of 0.13 m^3/s (3 mgd) was treated at the Ralph F. Brennan Water Treatment Plant for 30 days. An additional pilot plant run was later performed using an improved analog of XE-392, which is presently designated "XE-513".

Extensive analytical data were collected throughout the pilot- and plant-scale trials. A strict quality assurance program was developed for the study to assure maximum validity of data. A report on the results of each phase of the study is included in Appendix B. Results indicated substantial reductions in THM concentration, both immediately after chlorination and after a 24 hr. storage period used to approximate residence time in a distribution system. The correlation of TOC, TOX, and UV absorbance with total THMs was investigated in an effort to establish an easily performed process control test.

No secondary deterioration in water quality was noted from the experimental treatment scheme, and no major operational problems were experienced during the trial. The experimental coagulant system removed 50% more THM precursors than the conventional treatment methods used in the Daytona Beach Treatment Plants. Results of the pilot run using XE-513 indicated that lower doses of this polymeric coagulant could be used to achieve desired finished water quality. A cost estimate for use of the experimental treatment alternative was prepared.

This report was submitted in fulfullment of Cooperative Agreement No. CR 810676-01-0 by the City of Daytona Beach under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period May 12, 1983, through January 12, 1984, and work was completed as of August 1, 1984.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

Abs.	-- absorbance
Alum	-- aluminum sulfate
cm	-- centimeter
CU	-- color units
Ferric	-- ferric sulfate
GC	-- gas chromatograph
GC/MS	-- gas chromatograph coupled to mass spectrophotometer
Gal	-- gallon
gpm	-- gallons per minute
Km	-- kilometer
lps	-- liters per second
lpm	-- liters per minute
m	-- meter
ml	-- milliliters
MCL	-- maximum contaminant level - For purposes of this Study, MCL, when used to define a THM water quality goal, refers to a 0.1 mg/L (100 µg/L) contaminant concentration. When used in the context of water system THM compliance, however, MCL refers to the quarterly average THM concentration in the water distribution system.
MGD	-- million gallons per day
MLD	-- million liters per day
MTP	-- maximum total trihalomethane potential
mg/L	-- milligram per liter
NTU	-- nephelometric units
nm	-- nanometers
oz	-- ounces

pvc	-- polyvinyl chloride
RPM	-- revolutions per minute
RSD	-- relative standard deviation
s	-- second
SPC	-- standard plate count
THM	-- trihalomethane - For purposes of this Study, this is restricted to the following: Chloroform ($CHCl_3$), Bromodichloromethane ($CHCl_2Br$), Dibromochloromethane ($CHBr_2Cl$), Bromoform ($CHBr_3$)
THMFP	-- trihalomethane formation potential
TOC	-- total organic carbon
TOX	-- total organic halogens
Turb	-- turbidity
ug/L	-- microgram per liter
um	-- micrometer
UV	-- ultraviolet
w/v	-- weight per unit volume

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The cooperation of the personnel of the Ralph F. Brennan Water Plant and especially Mr. Dennis Colby, Manager, Water and Wastewater Plants Division, is gratefully acknowledged. The Authors also wish to express their gratitude to Mr. Lee Roby and Mr. Ed Parks for their significant contributions to the efficient execution of this project.

SECTION 1

INTRODUCTION

Water treatment methods used for the past 10 years in Daytona Beach, Florida, include lime softening for carbonate hardness reduction, coagulation using an anionic polyelectrolyte, fluoridation, chlorination to a free residual, and mixed media filtration. Water treated in this fashion meets standards set by the U. S. Environmental Protection Agency (EPA) under the authority of the Safe Drinking Water Act (PL 93-523) except for the trihalomethane (THM) maximum contaminant level (MCL).

The National Organics Reconnaissance Survey (NORS) of 1974 pointed out the widespread occurrence of THMs in drinking waters throughout the country. Sampling performed on the Daytona Beach system showed their presence in excess of 200 micrograms per liter (µg/L). Because of health concerns associated with this family of compounds, research was begun in 1976 in search of a treatment method to reduce THM concentrations through improvements in the existing treatment processes.

Three broad treatment options have been identified for reducing THM concentrations in drinking water: Removal of THM compounds after their formation, changing methods of disinfection to prevent their formation, and removal of the organic compounds (precursors) that form THMs upon chlorination.

Removal of precursors is generally the most attractive concept from a water quality standpoint, but it is not always possible to remove a large enough fraction to achieve sufficient THM reduction.

Previous projects (23) in Daytona Beach sponsored by the EPA looked at reducing THM concentrations by changing the point of chlorination and improving coagulation. While some THM concentration reduction in both instantaneous and stored samples was noted through the use of inorganic salts for coagulation, by far the most promising treatment scheme centered around the use of a new polymeric coagulant, XE-392 (Rohm and Haas Company).

The goal of this project was to determine the optimum use of the polymeric coagulant in a lime-softening plant. The three-phased approach that was used began with bench-scale testing to evaluate the effects of the coagulant by itself and in combination with other conventional coagulants. The most effective treatment methods developed from the bench work were next evaluated in a pilot plant. Pilot-scale results were then used to set conditions for a 30-day, plant-scale trial. On completion of the three-

phased program, an additional pilot-plant run using a newer, optimum version of XE-392 (XE-513, Rohm and Haas Company) was performed to determine whether this improved product would enhance THM removal at lower doses. Results of the extensive analytical monitoring performed throughout this project are summarized in this report.

SECTION 2

FINDINGS AND CONCLUSIONS

The following findings were observed during the pilot plant and plant-scale studies completed during this project:

1. Previous studies concluded that lime softening, with the addition of coagulants for turbidity control, will not remove sufficient THM precursors from the water studied to meet the MCL, assuming the practice of chlorination to a free residual was continued. This study confirmed this observation on a full-scale basis, but did not address the effect of softening process pH on THM precursor removal.

2. Storage pH and chlorine concentration were found to affect THMFP. When samples (chlorinated at a constant chlorine dose) were stored at higher pH, an increase in 24 hour THMFP was noted. An increase in 24 hour THMFP was also observed when samples (stored at a constant pH) were chlorinated at elevated doses.

3. Turbidity carryover from the treatment scheme evaluated was effectively removed by mixed media filtration to less than 0.45 NTU during the plant-scale trial.

4. Reductions in total organic carbon (TOC) and ultraviolet (UV) absorbance correlated well with reduction of THM concentrations. In general, reductions in THMFP concentrations were less than UV absorbance reductions but greater than TOC concentration reductions. The use of the UV absorbance correlation in particular may lend itself to the development of a continuous stream analyzer to monitor THM control practices.

5. Effluent THM concentrations from the EPA pilot plant were identical to those obtained during the full-scale trial at XE-392 doses of 18 mg/L (see Figure 1). The pilot unit may therefore be considered to simulate accurately the full-scale lime softening process at the Brennan Water Plant.

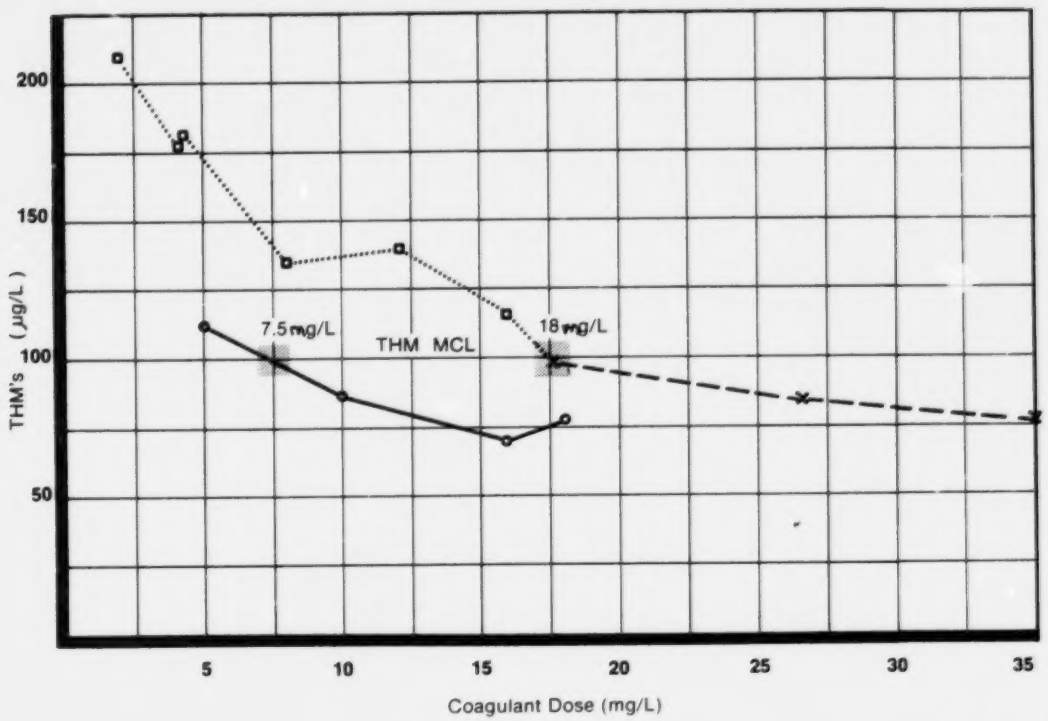


FIGURE 1. EFFECT OF EXPERIMENTAL COAGULANT DOSE ON FINISHED WATER THM CONCENTRATION

6. Adequately removing the floc formed when polymeric coagulants are used for precursor removal is extremely important. The system is sensitive to the coagulation, settling, and filtration processes, because the chlorinated floc produces THMs. Optimum coagulation also may reduce the dosages of coagulant necessary to achieve the required degree of precursor removal.

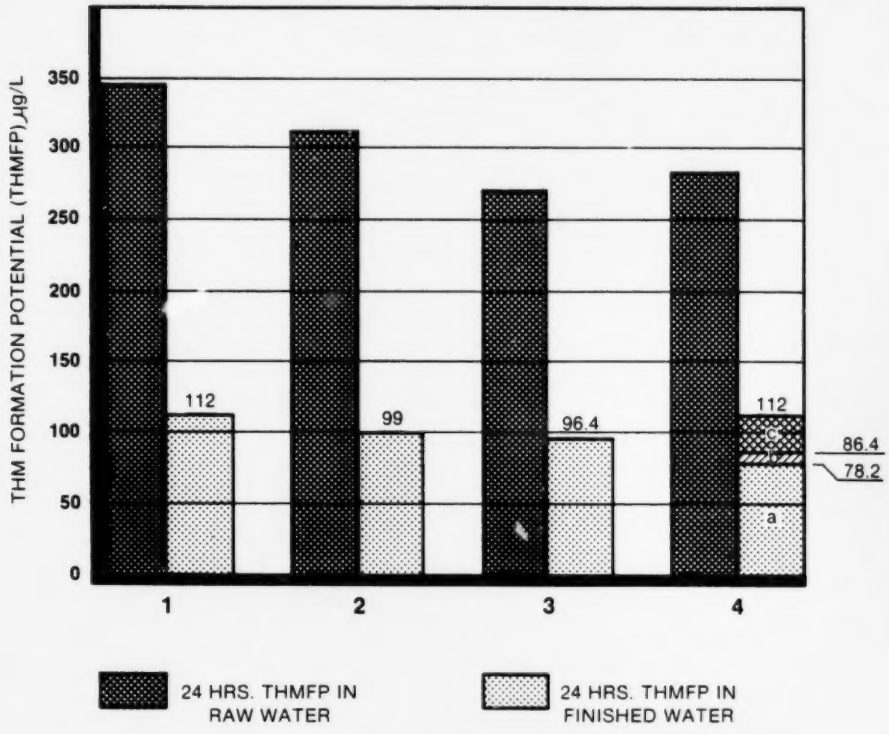
7. THM precursor removal using XE-513 was significantly better than that using XE-392 at similar doses. The analog product may indeed be considered an improvement as claimed by the manufacturer.

8. The inorganic coagulant dose required for use with XE-392 and XE-513 can be significantly reduced by judicious choice of a polyelectrolyte coagulant aid. The ferric sulfate, however, could not be entirely replaced by the polymers tested without a reduction in performance.

Based on the findings observed during this study, the following conclusions may be drawn:

1. Use of the Rohm and Haas polymeric coagulants in conjunction with lime softening reduced THM concentrations significantly more than did lime softening with conventional coagulants (Figure 2). Use of this material on a permanent basis would allow this system to meet the THM MCL, maintain chlorination to a free residual, and permit continuation of the algae control practice of chlorination before filtration.

2. The projected costs of using XE-513 for THM control in the Daytona Beach, Florida, system are too high to warrant its use on a continuous, full-scale basis. A more cost effective application of this material might be in systems where a low dosage could be used to replace high inorganic coagulant doses already in use for THM control, or possibly in systems where low XE-513 doses could be used to control seasonal fluctuations in THMFP.



CONDITION 1 - JAR TESTS, XE-392 20 mg/L
CONDITION 2 - PILOT PLANT, XE-392 17.7 mg/L
CONDITION 3 - PLANT SCALE TEST, XE-392 18 mg/L
CONDITION 4 - PILOT PLANT, XE-513

a - 18 mg/L
b - 10 mg/L
c - 5 mg/L

FIGURE 2. SUMMARY OF EXPERIMENTAL RESULTS
DAYTONA BEACH PROJECT 1983

SECTION 3

DESCRIPTION OF WATER SOURCE

A total of 15 wells, extending an average of 64 m into the Avon Park limestone formation (a portion of the Floridan aquifer) supply the source water for the Ralph F. Brennan Treatment Plant. Each well is 40.6 cm in diameter and cased to a depth of about 33.5 m. The remaining depth is an open hole in the solid limerock formation.

These wells are located in a line running roughly east to west from 5.6 Km to 14.5 Km from the Atlantic Coastline and then north approximately 1.6 Km. All wells feed into a common raw water main which supplies the Brennan Plant. They are located on a ridge called Rima Ridge, which separates two terraces. One of these, the Talbot Terrace, is a broad expanse of swampy land with an ill-defined drainage pattern. This is an area with a high recharge rate to the Floridan aquifer and the dark, tea-colored swamp water is apparently responsible for much of the color found in Daytona's raw water.

In passing through this swampy area, the water's pH is depressed, presumably by the naturally occurring weak organic acids such as humic, fulvic, and tannic acid, but then is neutralized as it migrates downward to the Floridan aquifer through underlying limestone formations. This neutralization process is responsible for the relatively high hardness and alkalinity found in the raw water; see Table 1 - Water Analysis. Raw water quality with respect to alkalinity and total hardness generally remains within a 10 percent variation; however, THMFP varies considerably on a seasonal basis as a function of rainfall and between individual wells as shown in Figures 3 and 4.

TABLE 1. Daytona Beach Raw Water Analysis, 1983

Parameter	Amount
pH	7.0
Color, CU	20.7
Turbidity, NTU	0.23
Total Hardness, mg/L as $CaCO_3$	295
Alkalinity, mg/L as $CaCO_3$	275
Iron, mg/L as Fe	0.31
24 Hr. THMFP, mg/L	0.305
TOC, mg/L	8.3
UV Absorbance, 254 nm.	0.242
TOX, mg/L	0.042

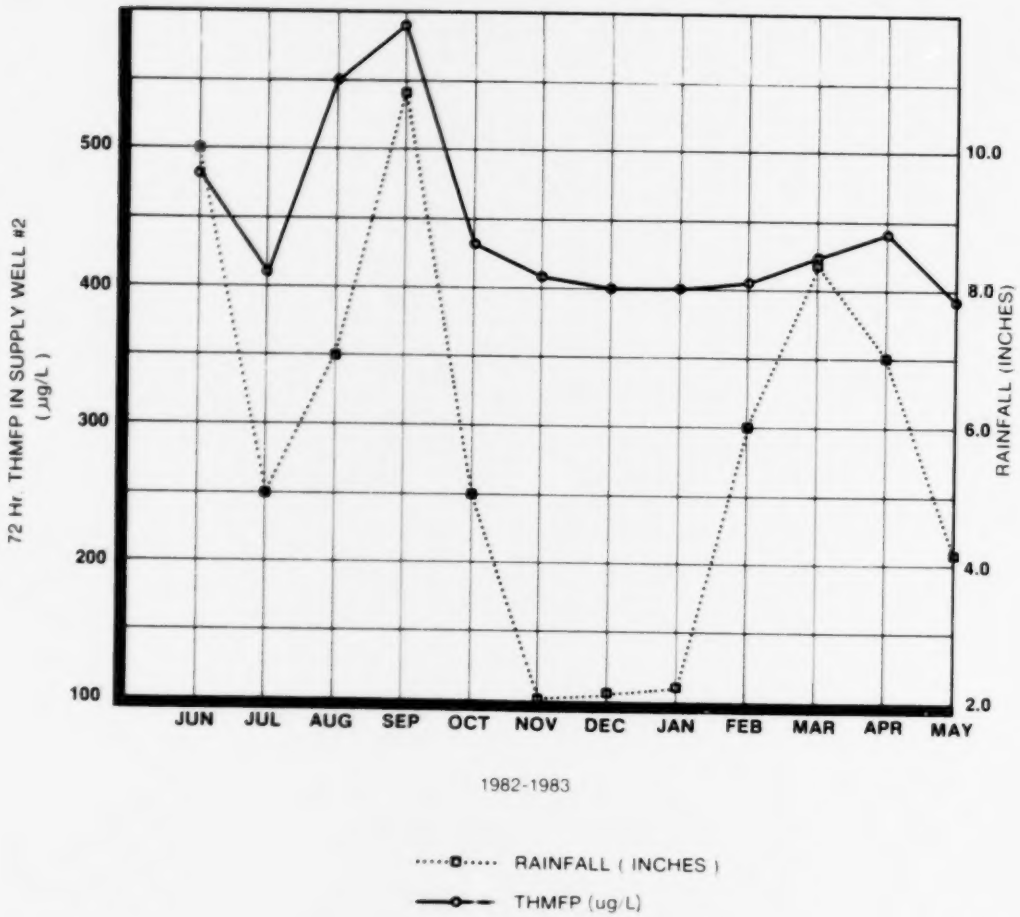


FIGURE 3. SEASONAL VARIATION IN THMFP WITH RAINFALL

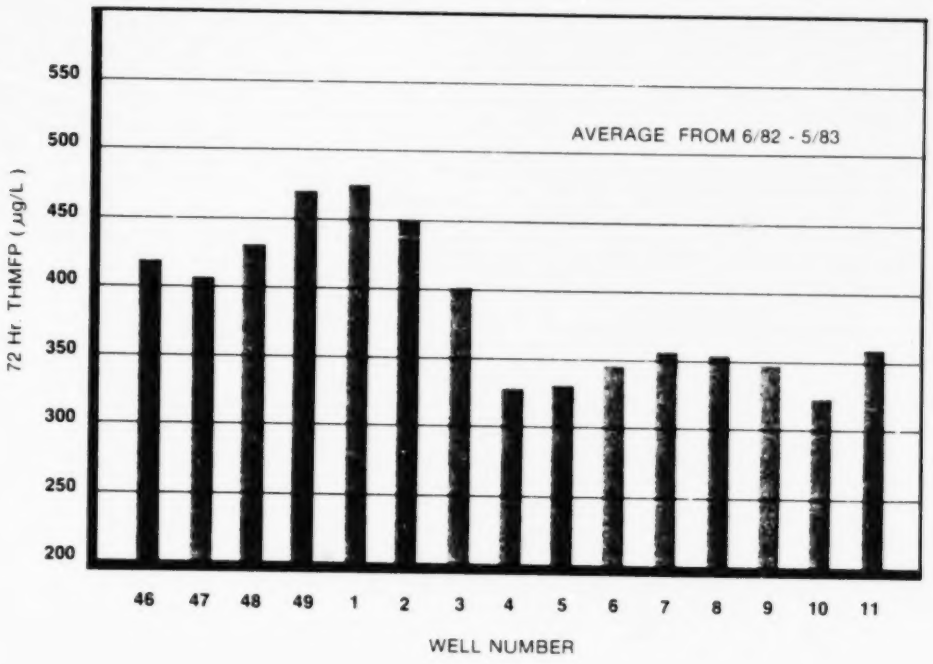


FIGURE 4. THMFP VARIATION IN DAYTONA BEACH RAW WATER SUPPLY WELLS

SECTION 4

BACKGROUND

REVIEW OF LITERATURE

The National Organics Reconnaisance Survey (NORS), conducted in 1974, identified the widespread occurrence of trihalomethane compounds in public water systems in the United States. In a report by Symons (1) in which the findings of this study were summarized, it was noted that at water plants where precipitative lime softening is practiced, THM concentrations are significantly higher than the average THM concentration found for other systems surveyed because of the pH dependency of the haloform reaction. This bears a special significance in Florida where the majority of public water systems use the lime softening process.

A review of the literature indicated three basic approaches may be taken toward control of trihalomethanes. Because precursors + chlorine leads to THMs, trihalomethanes can be controlled by removal of the precursors, replacement of chlorine with an alternate disinfectant, or removal of THMs after their formation.

Air stripping and adsorption are two well-documented techniques for removal of trihalomethanes (7). Corrosion rates in the distribution system may, however, be affected by the increased oxygen levels in the aerated water. Less volatile halogenated compounds, if formed during chlorination, are relatively unaffected by the air stripping process. Christman, et al. (6), noted that although THMs have received much attention in recent years, many other halogenated products are formed after chlorination of waters containing humic and fulvic acids, the health effects of which are relatively unknown.

Non-volatile, non-halogenated organics in the raw water are generally unaffected by air stripping. Carbon adsorption, although effective in removing a wide range of organics (2), is regarded as an expensive treatment method if used solely for removing THMs because of high regeneration and material replacement costs. Similarly, use of ion exchange resins appears very expensive for this application.

Alternate disinfectants used in Florida, if other than chlorine based (e.g., Ozone, UV contact), must be followed by a sufficient chlorine dosage to maintain a residual disinfectant in the distribution system (3). This would lead to increased chemical feed costs and possibly negate the positive effects of the alternate disinfectant, because by introducing chlor-

ine, additional THMs would likely be formed. The use of chloramine disinfection is the disinfectant of choice for meeting the THM MCL for many water treatment plants. In addition to concern over possible adverse health effects of chloramines (4,5), use of this process does not address the underlying cause of the THM issue, that of source water quality.

The third approach to THM control, removal of THM precursors, is not only attractive from the viewpoint of an overall improvement in water quality, but operationally may be desirable because at least one of the precursor removal techniques, coagulation, would not require extensive or expensive plant modifications to implement at Daytona Beach.

A number of investigators have looked at coagulation techniques for removal of THM precursors. Kavanaugh (8), Babcock and Singer (9), and Oliver and Lawrence (10), found inorganic coagulants to be effective in removing THM precursors in river, synthetic, and Great Lakes basin waters, respectively. Semmens, et al. (11), reported coagulation techniques selectively removed higher molecular weight compounds (humic acids) from water, but were relatively ineffective in removing the lower molecular weight fractions (fulvic acids). Alum and ferric sulfate were found to be equally effective in reducing precursor concentrations, while polymers were relatively ineffective when used by themselves. Bixby (14) stated that where fulvic acid is present in water, coagulation with alum is not effective for THM precursor removal.

Digiano (13) reported good THM precursor removal results when using a cationic polymer on a low alkalinity and low color water in New England. Chadik and Amy (12) found that alum worked better than ferric sulfate with respect to TOC and THMFP reductions at equivalent doses. Significantly, it was noted (23) that the precursors in a Daytona Beach ground water tested were not readily removed by coagulation with alum or ferric sulfate without use of a polymeric coagulant aid. Even then, coagulation alone was not sufficient to reduce the water's Maximum Total Trihalomethane Potential (MTP) concentration to less than 0.3 mg/L.

In general, the literature indicates coagulation can be an effective technique for THM precursor removal. The degree of effectiveness, however, is very site-specific with respect to the nature of the organic compounds to be removed, and to the choice of coagulants and the conditions to which they are applied.

GENERAL APPROACH

A three-phased plan was used in this project.

Phase 1. Bench Scale Laboratory Tests. This phase involved screening coagulants to be used in conjunction with lime softening for removal or reduction of THM precursor materials. The precursor removal potentials of inorganic coagulants, organic polyelectrolytes and clays, alone and in combination with XE-392, were evaluated.

Phase 2. Pilot Plant Evaluation. A mobile pilot plant loaned by EPA (see Section 6) was used to evaluate the most promising coagulant scheme identified in Phase 1. The pilot plant trial provided process data under dynamic conditions rather than the static conditions of the bench work.

Phase 3. Plant-Scale Evaluation. This 30 day trial involved side-by-side operation of two lime softening treatment units, one operating in a normal mode of softening with coagulation for turbidity control only, and the other operating under conditions evaluated in Phase 2.

SECTION 5

JAR TEST PROGRAM

PHASE I

Jar testing (refer to Appendix C for procedure) was performed with Daytona Beach raw water supplied from the Ralph F. Brennan Water Treatment Plant. The bench-scale program focused on optimizing coagulation in a treatment scheme that would reduce finished water THMs to 0.1 mg/L (100 µg/L) after 24 hr. storage to simulate distribution system conditions.

The first series of jars demonstrated the need for the XE-392. Alum or ferric sulfate of similar molarity was added to plant raw water at doses of 20, 30, 40, 50, 60 and 80 mg/L. Lime was then added to adjust final pH to 9.3. Following chlorination, pH was immediately adjusted to 8.3 with NaOH for storage. The most promising results were achieved using 60 mg/L doses for both alum and ferric sulfate. The ferric sulfate exhibited a slightly better THMFP removal - 26% compared to alum's 24% removal. Neither inorganic coagulant reduced THMFP concentration sufficiently, however, to approach the 100 µg/L effluent quality goal.

The next set of jars tested the performance of XE-392 with lime softened water adjusted to a pH of 9.3. Experimental coagulant doses ranged from 10 mg/L to 60 mg/L in increments of 10 mg/L. Coagulant was added after lime addition to pH 9.3. Details of the procedures used in jar testing are presented in Appendix C of this report. The optimum dose was determined to be 20 mg/L XE-392, resulting in 24 hr. THMs of 185 µg/L, or a 47% reduction of THMFP. Although precursor removal efficiency using XE-392 was double that using inorganic coagulants, final THMs and turbidities still exceeded their MCLS.

Routine filtration through Whatman #1 filter paper did not adequately capture the fine floc developed using XE-392. Increasing XE-392 doses, however, produced greater THMs. It was therefore suspected that the fine floc consisted of XE-392, which when chlorinated, produced THMs. This could not be confirmed, however, because a gel formed during solvent extraction which prevented THM analysis.

Previous work by the project team found the use of Ca 35, a bentonite clay, was necessary to improve turbidities after coagulation with XE-392. Jars were set up to compare the performance of alum at a 60 mg/L dose to ferric sulfate at a 60 mg/L dose, both in conjunction with a 5 mg/L clay dose and varying XE-392 doses. Again, ferric sulfate out-performed alum, resulting in THMFP reductions of 56% as opposed to 50%. The best results

were obtained with the following scheme: 5 mg/L Ca 35 clay, 20 mg/L XE-392, 60 mg/L ferric sulfate, and 220 mg/L lime. Immediately following chlorination, the pH was adjusted to 8.3 for storage.

Three different clays were compared with Ca 35. Four jars were set up to test four different clays. Each jar then received 20 mg/L XE-392, 60 mg/L ferric sulfate, and 220 mg/L lime (to pH 9.3). THMFP removals were 52%-54% for all clays tested, indicating similar performance. Because experimental quantities were on hand, the Ca 35 was selected for subsequent jar testing.

Kavanaugh (16) referred to the importance of obtaining proper pH for coagulation using ferric sulfate. A series of tests investigated coagulation at pH 5.0, 5.5, 6.0 and 6.5, followed by filtration through Whatman #1 filter paper prior to lime softening. Best THMFP removal was obtained at pH 5.0 (54%), the same as that obtained in previous jar testing when no attempt was made to adjust the jar pH. Since intentional lowering of pH did not produce improved results, subsequent jar tests were conducted at the non-adjusted jar pH of 9.3.

The next set of jar tests investigated the need for clay to control turbidity. Four jars were set up to compare different ferric sulfate doses without clay. The clay proved to be unnecessary.

Work was then directed toward identifying additional benefits that might be realized, i.e., low turbidities and THMs, through the use of polyelectrolytes with the XE-392 and ferric sulfate. A nonionic polymer,* was being used at the Brennan Plant and therefore was selected for the next set of six jars. Ferric sulfate doses used were 10, 20, 30, 40, 50 and 60 mg/L, distinguishing the six jars. All jars received 20 mg/L XE-392, 220 mg/L lime (to pH 9.3) and 1 mg/L of the polymer.* Immediately following chlorination, pH was adjusted to 8.3 for storage. By using the polymer, the optimum ferric sulfate dose was reduced to 10 mg/L, resulting in a 24 hour THM concentration of 96 µg/L, a 71% THMFP concentration reduction. Final turbidity averaged 0.65 NTU. The MCL for turbidity and the effluent quality goal for THMs had finally been achieved.

Further testing compared the results of the nonionic polymer* with an anionic polymer,** cationic polymer*** and a second nonionic polymer.**** Under the same testing conditions, the nonionic and anionic polymers performed equally using a 10 mg/L ferric sulfate dose and achieved a 71% THMFP concentration reduction. Final turbidities using the nonionic polymer were slightly better than with the anionic polymer, although both polymers produced water with a turbidity less than 1.0 NTU. The nonionic and the cationic polymers produced similar THM results. For both polymers optimum results were obtained when used with 20 mg/L ferric sulfate. Approximately 64% THMFP concentration reduction was achieved.

* L650E - Calgon Corp.
** Nalcolyte 8184 - Nalco Corp.
*** Cat Floc T - Calgon Corp.
**** Magnifloc 985N - American Cyanimid Co.

Optimum nonionic polymer dose was investigated in the next set of 6 jars. Doses of 0.01, .05, 0.1, 0.5, 1.0 and 1.5 mg/L of nonionic polymer were added to water treated with 10 mg/L ferric sulfate, 20 mg/L XE-392 and 220 mg/L lime (to pH 9.3). Following chlorination, pH was adjusted to 8.3 for storage. The 1.0 mg/L and 0.01 mg/L polymer doses resulted in the lowest THMFP - 112 µg/L and 107 µg/L respectively. Using a 0.01 mg/L polymer dose, however caused final turbidity to exceed 1.0 NTU as opposed to a final turbidity of .74 NTU obtained using a 1.0 mg/L polymer dose.

In all of the jar testing described thus far, reagent grade ferric sulfate was used. For pilot plant and full scale studies, a 48% ferric sulfate***** solution was used. A set of jars comparing the commercial ferric sulfate solution to reagent grade ferric sulfate indicated equal performance. In all cases, pH was controlled to 9.3 using lime, then adjusted to 8.3 for storage immediately following chlorination.

Based on the bench scale testing, a treatment scheme for the pilot plant phase of the study, Phase II, was developed. A decision was made to dose ferric sulfate at 10 mg/L, XE-392 at 20 mg/L, and nonionic polymer at 1.0 mg/L. Raw water would be lime softened at a pH 9.3 using approximately 220 mg/L Lime dose as in the full scale process at the Brennan Plant. Pilot plant effluent would then be chlorinated and pH adjusted to 8.3 for storage.

PHASE II - PILOT PLANT JAR TESTING

While operating the pilot plant during Phase II of the Study, iron carryover from the clarifier was observed. Effluent iron concentrations ran as high as 0.93 mg/L. This was a serious concern because the secondary MCL for iron in drinking water is 0.3 mg/L. It was suspected that the source of iron was pilot plant corrosion. To test this hypothesis, two jars were run as duplicates to simulate pilot plant conditions. Results indicated the iron source was indeed corrosion in the pilot plant itself, particularly the clearwell, as earlier hypothesized.

ADDITIONAL JAR TESTING

Ferric Sulfate Dose

Previous jar testing did not evaluate ferric sulfate doses less than 10 mg/L. A set of six jars were treated with lime to pH 9.3, 20 mg/L XE-392, 1.0 mg/L Calgon 650E, and varying doses of ferric sulfate: 0.0, 2.0, 4.0, 6.0, 8.0, and 10.0 mg/L. Filtered effluent from all six jars when chlorinated and pH adjusted to 8.3 had THM concentrations less than 100 µg/L. Lowest THM concentrations resulted from the 2.0 mg/L ferric sulfate dose. The jar without ferric sulfate had a pre-filtration turbidity of 45 NTUs as compared to 17 NTUs with the 2.0 mg/L dose. The fine floc causing the 45 NTUs was filterable through a .45 micrometer membrane filter, resulting in an acceptable turbidity of .44 NTUs.

***** Leachem Industries, Inc.

Based on this test, the need for an inorganic coagulant was apparent. The optimum ferric sulfate dose appeared to be less than or equal to 2.0 mg/L. A sample dosed with XE-392 and polymer provided a 76% THMFP concentration reduction. Finished water THMs of 67 µg/L produced in jar tests at this reduced ferric sulfate dose were below those seen in the pilot and plant scale trials where higher ferric sulfates doses were used.

SECTION 6

PILOT PLANT DESCRIPTION

The pilot plant used in this study was a 0.63 lps. water treatment facility belonging to the U. S. Environmental Protection Agency. The general layout of the pilot plant is shown in Figure 5. Housed within the 13m (42 feet) long trailer are two identical water treatment systems constructed of stainless steel. These two water systems may be run independently or in series. During this project only one treatment system was needed.

Raw water was provided via a 5 cm polyvinyl chloride (pvc) line from the Brennan Plant raw water supply. A booster pump delivered incoming raw water to a constant head tank. The water was then transferred through valves and a flow meter for flow adjustment (0.315 lps) to the rapid mix tank, then to four flocculation chambers in series, providing a total detention time of approximately 40 minutes. Flocculation chambers were followed by a clarification tank providing 4.4 hours detention time. The settled water was then pumped from a collection box to two pressure filters containing sand and anthracite. Filtered water then entered the clearwell.

Conditions and chemical doses used in the pilot plant runs were based on optimum jar testing results determined in Phase I of this study. A more detailed description of the pilot plant is provided in Appendix D.

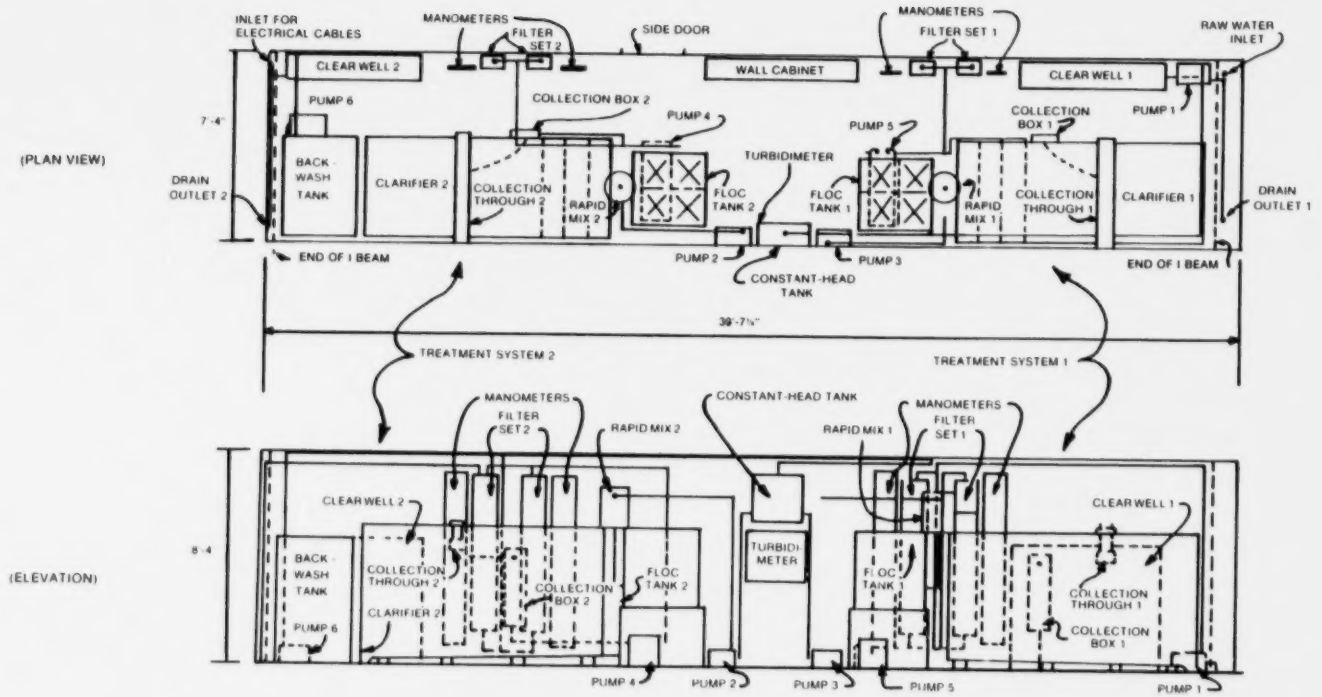


FIGURE 5. GENERAL LAYOUT OF TRAILER-MOUNTED PILOT PLANT

SECTION 7

PILOT PLANT OPERATIONS

Two pilot plant runs were performed during this study. The first run evaluated the experimental coagulant XE-392. A second run was performed to test the analog coagulant XE-513.

RUN #1: XE-392 STUDY

The pilot plant study was started on August 8, 1983. Brennan Plant operators and laboratory technicians assisted in the monitoring and maintenance required for 24 hour operation. Chemical preparation and feed points were set-up based on jar test results. Figure 6 is a diagram of the pilot plant set-up used during this run.

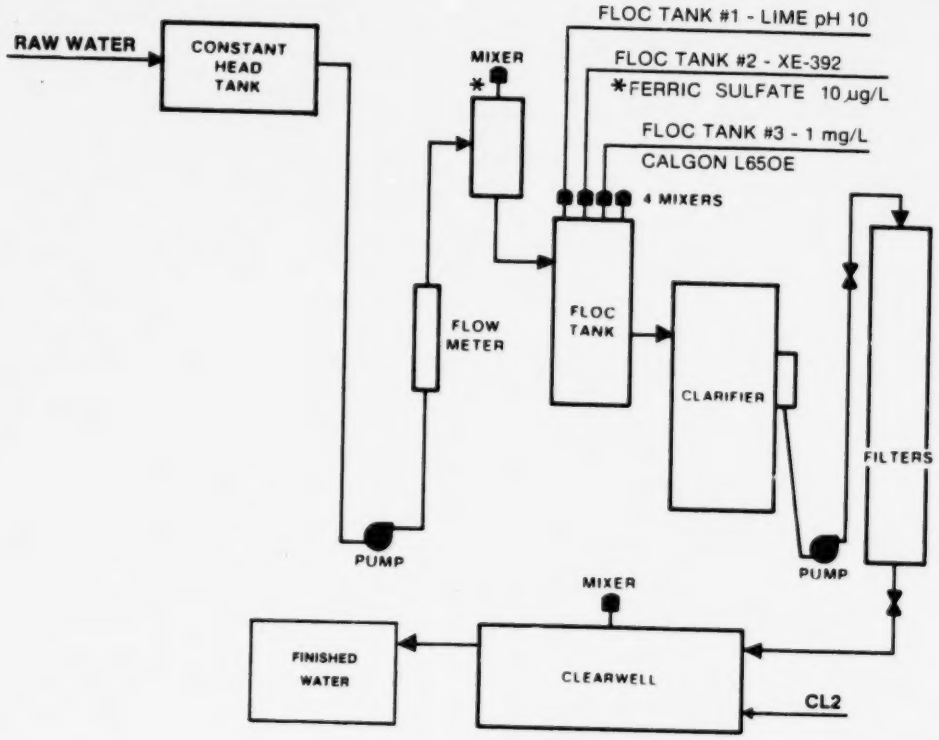
The following paragraphs describe the chemicals and dosing procedures used:

1. LIME: Slaked lime from the Brennan Plant slakers was hand carried to a 324L (35 gallon) container in the pilot plant. A recirculating system kept the lime slurry in suspension. A peristaltic pump delivered the lime from the recirculating system to floc tank #1. The pH was checked hourly and pump adjustments were made to maintain a pilot plant effluent pH of 8.0-8.5.

2. POLYMERIC COAGULANT (XE-392): A stock solution of known % solids was diluted with tap water to the desired concentration. A diaphragm pump metered the diluted XE-392 to floc tank #2. Doses of 17.7, 26.6, and 35.4 mg/L XE-392 were used.

3. FERRIC SULFATE: A 48% ferric sulfate solution was diluted with tap water to a final concentration of 0.48%. The dilute solution was pumped to floc tank #2 with a diaphragm pump. A 10 mg/L ferric sulfate dose was maintained for all pilot plant work.

4. POLYMER (Calgon L650E): A 1% polymer solution from the Brennan Plant polymer system was hand carried to a container located along side the pilot plant. A peristaltic pump delivered a set volume to an eductor type mixing device where it was diluted with a 3.785 l/min flow of Brennan plant effluent. The resulting solution



XE-392 DOSES: 17.7, 26.6, 35.4 mg/L

* LAST 3 DAYS OF RUN
FERRIC SULFATE POINT OF ADDITION
CHANGED TO RAPID MIX TANK

FIGURE 6. PILOT PLANT SET-UP USED DURING RUN NO. 1

was pumped to floc tank #3 using a diaphragm pump. A 1 mg/L dose of polymer was applied.

5. CHLORINE: Chlorine gas was fed by an injector system to the clearwell. Feed was controlled by a chlorinator mounted on a 50 lb cylinder. Adjustments were made to maintain a 2.5-3.5 mg/L free chlorine residual in the pilot plant effluent.

Pilot plant effluent pH and chlorine residual were monitored hourly. Daily samples were collected when finished water pH was 8.0-8.5 and a minimum chlorine residual of 1.8 mg/L was present. Sample collection points were: raw water, clarifier effluent, filter effluent, and clearwell effluent. Sample frequency, location and laboratory analyses performed are summarized in Table 2.

Maintenance problems were minimal during this phase. Daily calibration of chemical pumps revealed occasional feed rate deviations. Filters were washed when flows could not be adjusted to 0.016 lps. This resulted in backwashing approximately every four days.

The pilot plant sludge withdrawal system was inadequate for controlling the clarifier sludge blanket. Sludge removal was possible only after draining the tanks at the end of the run and forcing the sludge out with a pressure hose. This was not caused by the experimental coagulant, however, because similar problems were encountered during previous studies using this pilot plant for lime softening alone.

RUN #2: XE-513 STUDY

The pilot plant was started up November 30, 1983, and run continuously until December 15, 1983 to evaluate performance of XE-513, an improved analog of XE-392. Chemical preparation and feed systems were identical to that used during Run #1. Points of chemical addition were changed, however, to simulate the previous full scale run as is shown in Figure 7. During this run, XE-513 was added to the rapid-mix chamber; slaked lime and 10 mg/L ferric sulfate added to floc tank #1; and 0.1 mg/L Calgon L650E added to floc tank #3.

The purpose of testing XE-513 was to compare it with XE-392. Because an XE-392 dose of 18 mg/L was optimum during the full scale trial, an initial XE-513 dose of 18 mg/L was used during Run #2. XE-513 doses of 16, 10 and 5 mg/L were also tested. The polymer dose of 0.1 mg/L was chosen, based on results of full scale testing.

RESULTS

The initial XE-392 doses selected were 20, 15 and 10 mg/L as dictated by the jar testing results. However, it was discovered after performing the initial pilot run that the stock XE-392 solids content was nearly double that used for jar testing. Using the correct solids content, calculations revealed the doses were actually 35.4, 26.6, and 17.7 mg/L XE-392 respectively.

TABLE 2

ANALYSES PERFORMED DURING PILOT TESTING

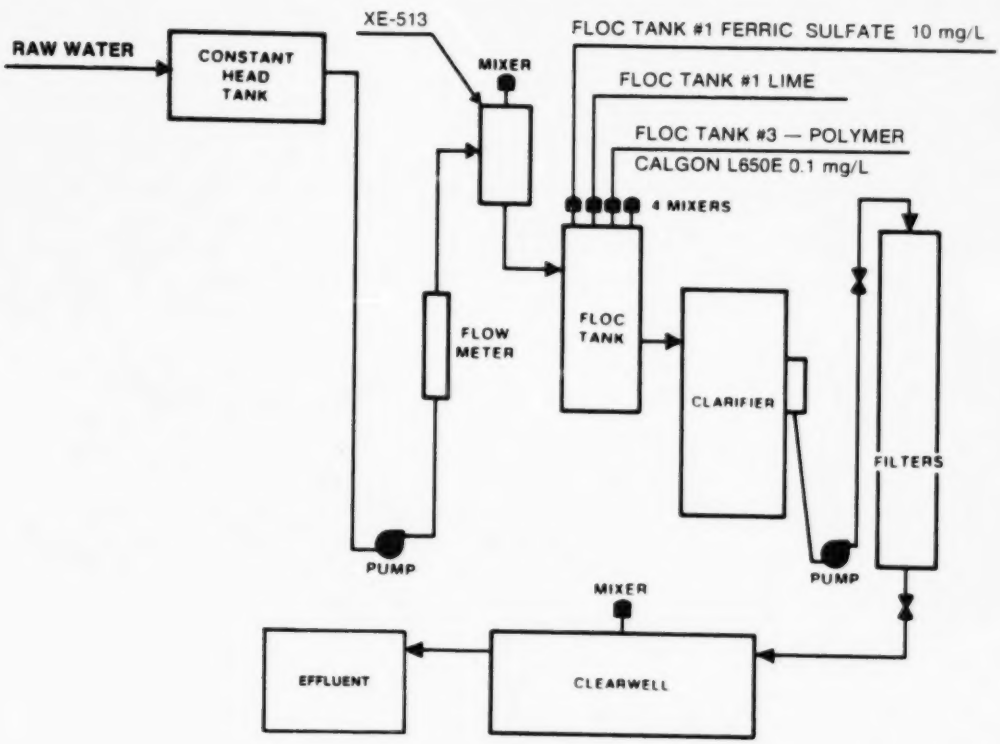
ANALYSES* PERFORMED DAILY

	Raw	Clarifier Effluent	Filter Effluent	Plant Effluent
Initial THM	X			X
24 Hr. THMFP	X			X
pH	X	X		X
Total Hardness	X			X
Alkalinity	X			X
Color	X	X		X
Turbidity	X	X		X
TOC	X			X
UV	X		X	

ANALYSES PERFORMED ONCE DURING RUN

THM Formation Curve	X			X
GC/MS	X			X

* Refer to Appendix A for test procedures.



XE-513 DOSES 5, 10, 16, 18 mg/L

FIGURE 7. PILOT PLANT SET-UP USED DURING RUN NO. 2

As predicted from the jar tests, the 17.7 mg/L dose resulted in a 69% THMFP concentration reduction and an average of 98.8 µg/L THMFP, just meeting the 100 µg/L MCL. Increased doses of 26.6 µg/L and 35.4 µg/L of XE-392 provided THM reductions of 76% and 77% respectively, as shown in Figure 8.

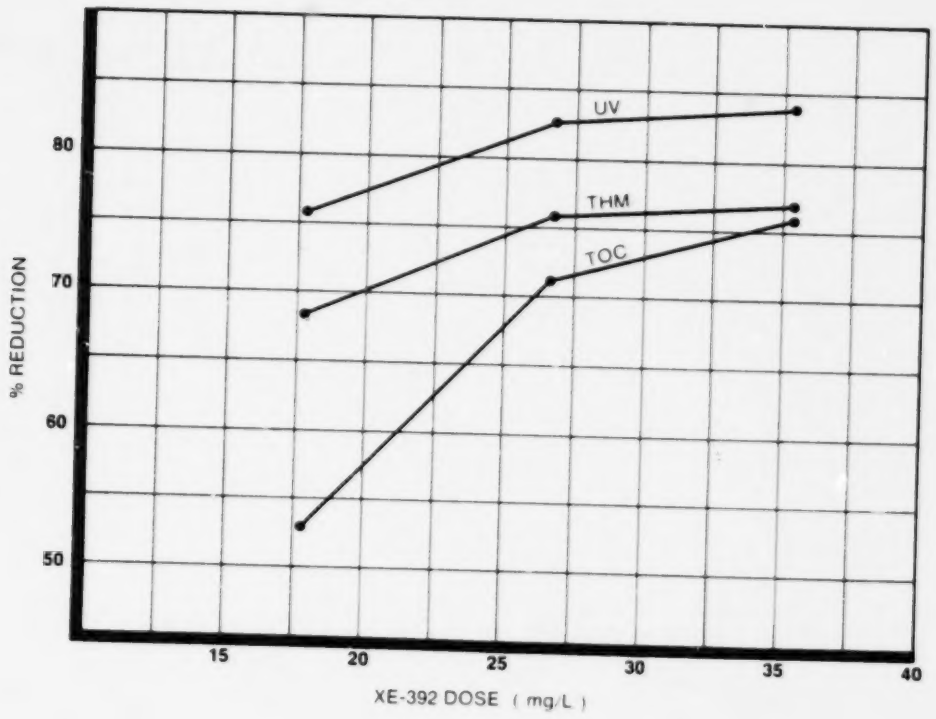
UV absorbance and TOC data followed the same trend as 24 hour THMFP; the % reduction increased with greater XE-392 doses. UV absorbance measurements were taken on chlorinated effluent and unchlorinated effluent samples.

The pilot plant, operating at the 17.7 mg/L XE-392 dose, provided the following water quality:

Parameter	Average Results
THM (24 hr. stored)	98.8 µg/L
UV abs.	.058 abs. units
TOC	3.7 mg/L
Color	.5 CU
Turb.	.09 NTU

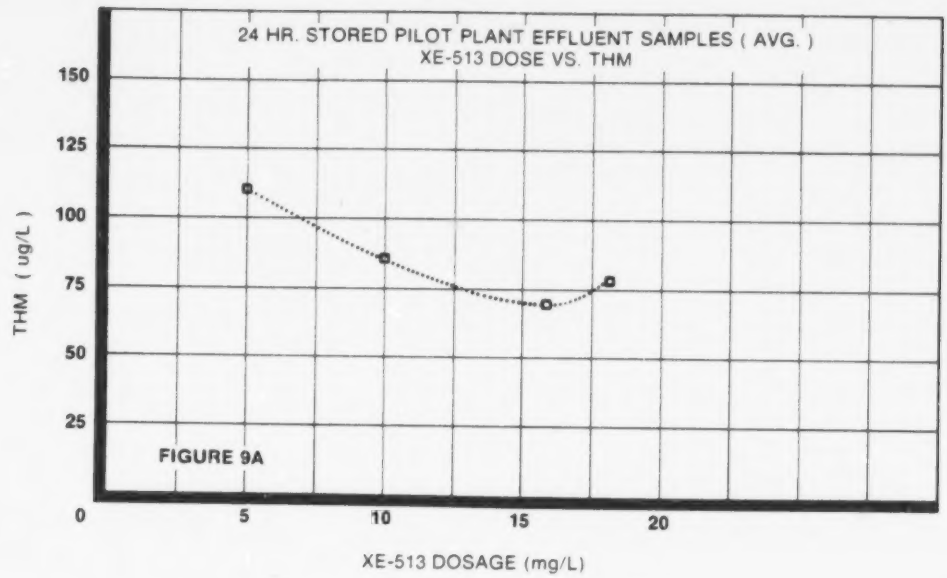
A correlation between pilot plant effluent UV absorbance and 24 hour THMFP is illustrated in Figure 9. This figure illustrates the relationships between UV and XE-513 dosage and THM and XE-513 dosage. Comparison of the two graphs illustrates that these relationships are similar and hence suggest that a UV correlation exists.

The results of pilot plant Run #2 (Table 3) showed improved performance with XE-513. A 10 mg/L XE-513 dose resulted in 86.4 µg/L THM as opposed to the 17.7 µg/L XE-392 dose which produced 98.8 µg/L THMs. The four-point dose curve developed from this run (Figure 9A), suggests a dose of 7.5 mg/L XE-513 may prove to be sufficient for meeting the 100 µg/L THM concentration goal.



PILOT PLANT RUN #1

FIGURE 8. EFFECT OF XE-392 DOSE ON PILOT PLANT EFFLUENT THMFP REDUCTION



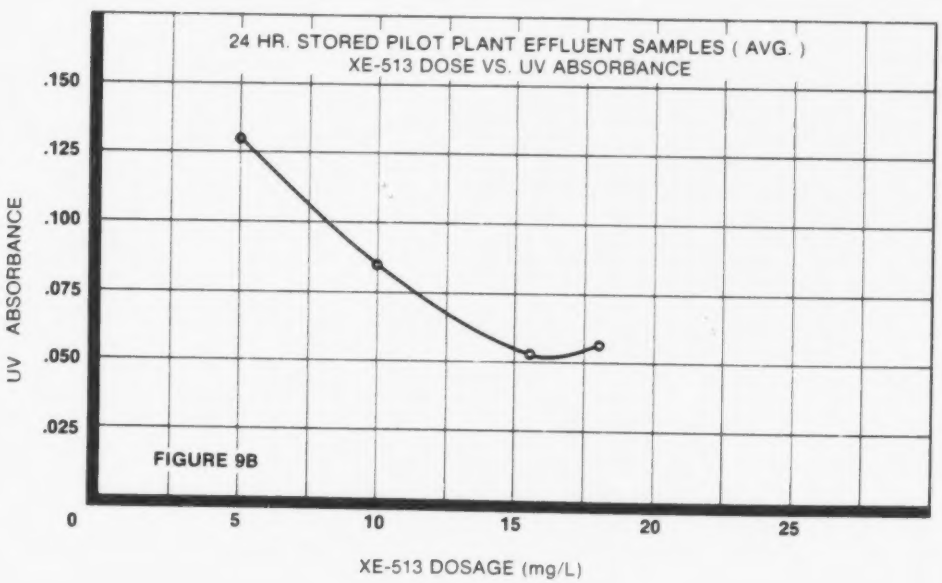


FIGURE 9. COMPARISON OF PILOT PLANT EFFLUENT THM AND UV ABSORBANCE AT VARIOUS XE-513 DOSES

TABLE 3

COMPARISON OF XE-392 and XE-513 PERFORMANCE

PILOT PLANT RUN #1: XE-392

AVERAGE VALUES

Dose XE-392	TOC (mg/L)		24 Hr. THM (µg/L)		UV Abs. (@254nm)		
	Raw	Effluent	Raw	Effluent	Raw	Effluent	Effluent*
35.4 mg/L	7.35	1.85	327	76.8	.249	.040	-
26.6 mg/L	7.5	2.2	338	82.3	.245	.038	.042
17.7 mg/L	7.8	3.7	312	98.8	.244	.044	.058

PILOT PLANT RUN #2: XE-513

AVERAGE VALUES

Dose XE-513	24 Hr. THM (µg/L)		UV Abs. @254 nm	
	Raw	Effluent	Raw	Effluent
18 mg/L	281	78.2	.236	.055
16 mg/L	251	69.6	.231	.052
10 mg/L	230	86.4	.242	.084
5 mg/L	254	112	.251	.128

* Effluent sampled after filtration, upstream of chlorination.

SECTION 8

PLANT-SCALE TRIAL

DESCRIPTION OF PLANT TRIAL

After reviewing data collected from the pilot plant trial, a meeting was held in Daytona Beach with the project officer, representatives of Florida Department of Environmental Regulation (DER) and the project team to agree on conditions for the 30 day plant-scale trial. A monitoring program was devised as represented in Table 4.

The trial began by establishing base-line conditions for the treatment plant. Figure 10 describes the flow of the Brennan Water Plant. One of two upflow clarifiers was dosed with 10 mg/L ferric sulfate just after the point of lime addition. After three days of operation in this mode, XE-392 was added at a 1.9 mg/L dose to the clarifier receiving ferric sulfate. This dose was increased incrementally every three days until results indicated the THM concentration of the clarifier effluent (after filtration, chlorination and storage) met the project goal of less than 100 µg/L.

Throughout the trial, flow through each of the clarifiers was held at a constant 0.13 m^3/sec (3 MGD). Therefore, the final product water leaving the Brennan Plant reflected a 1:1 dilution of water treated with XE-392. This water, in turn, was combined in the distribution system with an average daily flow of 0.26 m^3/sec (6 MGD) treated by the second Daytona Beach treatment plant.

The analytical work performed during the plant trial was very similar to that done during the pilot plant except that several additional analyses were performed. To ensure the bacteriological integrity of finished water, standard plate count and total coliform tests were run daily on plant influent and effluent samples. Samples were collected weekly from over 20 points in the distribution system for bacterial analysis. Sludge samples from each of the clarifiers were collected, and tests for settleable, total, and volatile solids were performed. Samples from the sludge thickener basin and cake from the vacuum filter were checked daily to determine solids concentration.

TABLE 4

MONITORING PROGRAM - PLANT SCALE TRIAL

SAMPLE LOCATION	PARAMETER MONITORED	MONITORING FREQUENCY
Raw Water	Flow	Continuous Recording
	THMFP, TOC, UV Absorb., SPC, Coliform	Daily
	pH, TH, ALK, Color, Turb	Twice Daily
	THM Formation Curve, GC/MS	Once During Trial
Settled Water	Flow (from each unit)	Continuous Recording
	THMFP, pH, TH, ALK, Color, Turb	Twice Daily
	Iron, TOC, UV Absorb., Sludge-Settlables, % Solids, Volatile Solids	Daily
Total Plant Effluent	Flow,	Continuous Recording
	THMFP, pH, TH, ALK	Twice Daily
	Color, Turb, Chlorine Residual	
	Iron, TOC, UV Absorb., SPC, Coliform	Daily
	THM Formation Curve; GC/MS	Once During Trial
Distribution System	Iron, Coliform, SPC, THM	Once Per Week

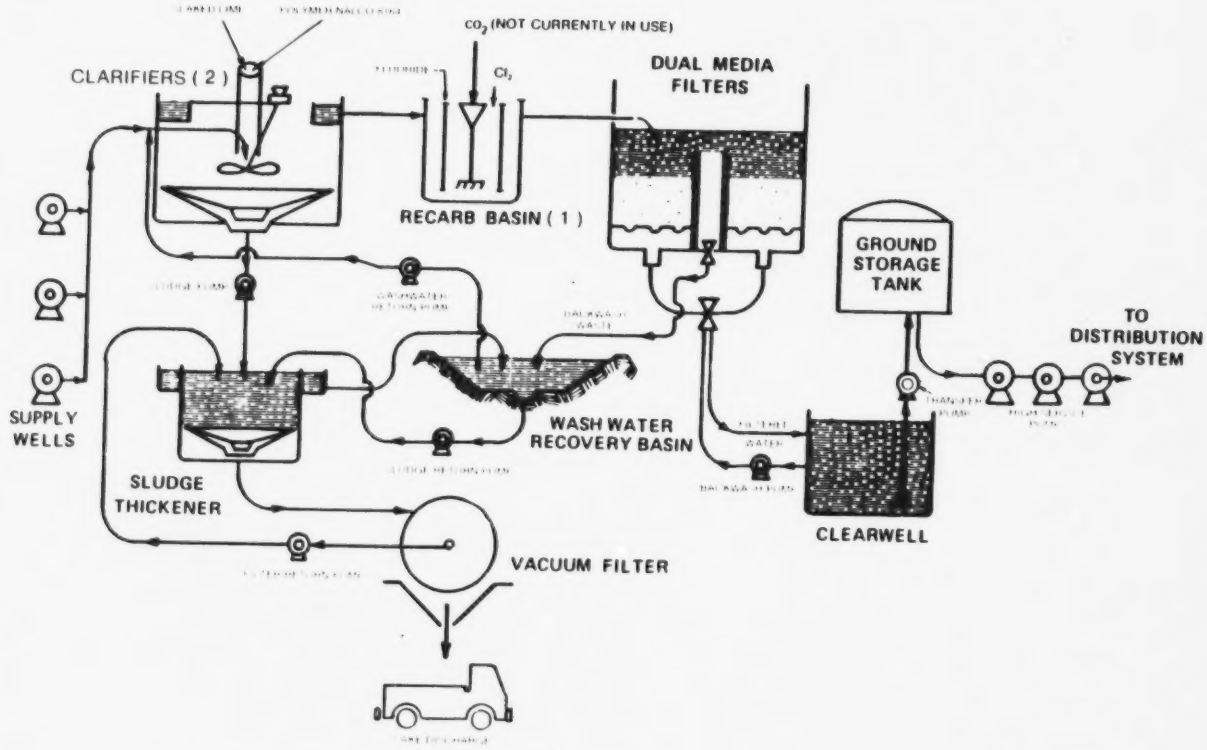


FIGURE 10. FLOW DIAGRAM OF RALPH F. BRENNAN WATER PLANT
DAYTONA BEACH, FLORIDA

RESULTS

Very early in the experiment a problem was experienced because the point of chlorination was changed from the recarbonation basin to the plant clearwell. Under usual conditions chlorine is added prior to filtration in the Brennan Plant. This controls algae growth within the filters as well as stabilizes the high pH water after softening. This is a very effective stabilization technique as evidenced by the low amount of carbonate build-up on the filter media during the Brennan Plant's 10 years of operation.

Work performed during a previous study, however, indicated that chlorinating upstream of the filters resulted in higher THM concentrations than would be formed if chlorination took place in the plant clearwell. This is to be expected because the filtration process removes some precursor material associated with the suspended turbidity particles. Soon after moving the chlorination point, unusual head losses were noted in the high rate filters. Upon backwashing the filters it became apparent that the source of the problem was hydrogen sulfide (H_2S) leaving solution during the pressure drop through the filters.

Pockets of H_2S formed in this manner caused a condition similar to air binding in the filters, effectively shortening filter runs. Because this plant had no other provisions for H_2S control, the chlorination was returned to its original point of application, the recarbonation basin. This immediately eliminated the problem. It was recognized, however, that this action would have the effect of increasing plant effluent THM concentrations compared to what might have been produced under more optimal chlorination conditions.

During the four days that ferric sulfate was added without XE-392, a negligible 3% difference in THMFP between the test and control clarifier (22.6% reduction compared to raw) was noted, indicating that very little precursor removal capability could be attributed to the use of ferric sulfate on this water. UV absorbance and TOC also indicated no difference in performance between clarifiers.

During the fourth day of the trial, 1.9 mg/L XE-392 was added to the test clarifier with ferric sulfate. This mode slightly, but consistently outperformed the control. A 9.5% difference in THMFP removal, 1.2% UV absorbance difference, and 4.9% TOC difference were observed.

Increasing the XE-392 dose to 3.8 mg/L produced further reduction in THM concentrations, UV absorbance, and TOC. When the XE-392 was increased to 8 mg/L, the differences between water produced in the two clarifiers became more pronounced. The THMFP from the test clarifier was 31.5% less than from the control. UV absorbance reflected a 35.9% difference and TOC, 20.3%. When compared to raw water, the effluent from the test clarifier showed reductions of 54.8% for THMFP concntrations, 61.1% for UV absorbence, and 32.8% for TOC.

Turbidity and color carryover problems developed quite unexpectedly when the XE-392 dose was increased to 12 mg/L. Also, a marked drop in floc

size and settling characteristics was noticed. An attempt to increase floc size by adjusting polymer dose rate met with some success. It was observed, however, that the color of the water filtered through Whatman #1 paper increased from 0 CU to 10 CU. No comparable increases in either color or turbidity were observed in plant effluent at this time. This indicated that the visibly different floc formed at the 12 mg/L XE-392 dose was removed by the Brennan Plant mixed media filters but was passing through Whatman #1 filters during lab filtration. In the process, color (presumably entrapped in the floc particles) was released.

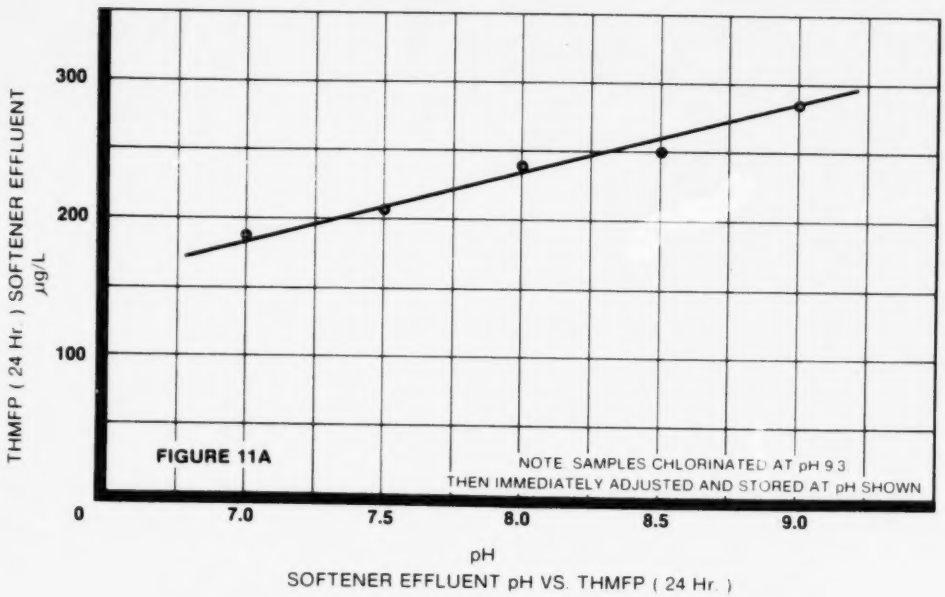
Clarifier effluent samples, filtered through 0.45 micrometer membrane filters and then analyzed, indicated significantly lower color values for the test clarifier. Control clarifier color values for membrane filtered samples were virtually the same as those obtained using Whatman filter paper. Test clarifier THMFP, when membrane filters were used, was consistently less than that measured when Whatman filters were used on samples split from the same clarifier.

Control clarifier samples had no appreciable variation in color or THMFP attributable to differences in filtration method. The average THMFP of the control and test clarifier effluents, when membrane filtered, compared very closely with Brennan Plant effluent THM concentrations. This result was expected, because plant effluent reflects the mix of the two waters.

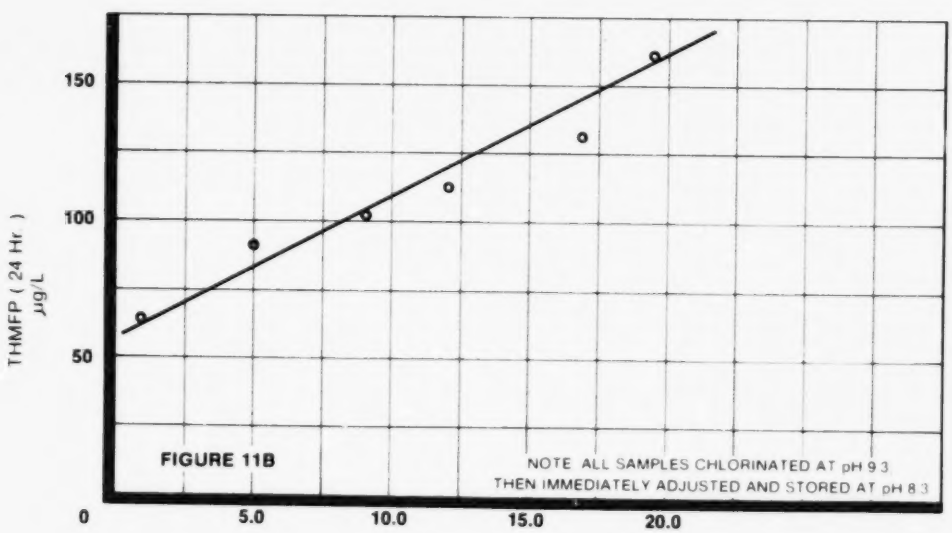
A review of the literature revealed that other researchers (17,18) routinely used a 0.45 μm membrane filter in their THM work. Because membrane filtered samples were shown to more closely approximate plant conditions, filtration through a membrane filter became the method of choice for the remainder of this study.

An increase of the XE-392 dose to 16 mg/L produced further differences between the test and control in THMFP, UV absorbance and TOC. The project goal of producing a chlorinated water with less than 0.100 mg/L THM was not met, however, until the polymeric coagulant dose was increased to 18 mg/L. At this dose, the test clarifier produced a water with an average THM concentration of 96.4 μg/L after 24 hour storage at a pH of 8.3. In comparison, THMFP of the control (at the same pH) was 207 μg/L. UV absorbance was reduced from .191 in the raw water to .042 in the test clarifier and TOC concentration was reduced from 7.4 to 4.6 mg/L.

Jar tests performed during phase one of this project revealed the relationship between pH and THMFP and between residual chlorine present during sample storage and THM as shown in Figure 11. While the pH vs. THM relationship for this water is an interesting one, there is little margin for adjustment of Brennan Plant pH. Stabilization practices call for maintenance of plant effluent pH in the 8.3 to 8.4 range for corrosion control. Accordingly, with the exception of the jar test samples used to develop Figure 11A, clarifier effluent samples were pH adjusted as necessary after chlorine addition to the pH range of 8.3 to 8.4.



SOFTENER EFFLUENT pH VS. THMFP (24 Hr.)



CHLORINE RESIDUAL VS. THMFP-JAR TEST SAMPLES AFTER SOFTENING

FIGURE 11. RELATIONSHIP BETWEEN THMFP AND SOFTENER PH AND RESIDUAL CHLORINE

The effect of chlorine residual on THM formation provided some difficulty during this project. Excess chlorine residuals clearly contributed to high THM values, but it was extremely difficult to predict the minimum chlorine dose necessary to maintain a free chlorine residual during the plant-scale trial. Because of the large number of samples processed during this project it was impractical to routinely use multiple chlorine doses for each sample. Two doses were used on most of the samples collected. Whenever a free chlorine residual was not present, THM results from the higher chlorine dosed sample were recorded. Samples with no chlorine residual were analyzed, however, to check adequacy of chlorine doses. When a free residual was present in both samples, the lower chlorine dosed THM results were used.

Sludge samples collected throughout the plant scale trial revealed that a slightly higher concentration of solids was maintained in the test clarifier (Table 5). This could not be positively attributed to test conditions however, because mechanical problems in the control clarifier frequently led to higher sludge removal rates than in the test clarifier. Volatile solids analyses indicated that sludge samples from the test clarifier contained more than twice the organic content found in the control. THM data on the sludge samples was inconclusive because of an unknown interference to the liquid-liquid extraction procedure used during this project. This interference was not present in sludge collected from the control and was only present in the test clarifier sludge at XE-392 doses above 8 mg/L.

Sludge produced during the test appeared to have no adverse dewatering properties as evidenced by a comparison of vacuum filter sludge cake percent solids both before and during the trial. A comparison of test and control sludge characteristics is presented in Table 5.

TABLE 5

LIME SLUDGE PROPERTIES - PLANT SCALE TRIAL

	Control Clarifier	Test Clarifier
Settlable Solids (mg/L)	611	847
Total Solids (%)	18	24
Volatile Solids (%)	0.3	0.7
24 Hr. THMFP Extracted (µg/L)	322	Unable to determine

TABLE 5 (CONTINUED)

	During Trial	Average (one month before, one month after trial)
% Solids Feed to Vacuum Filter	19.9	23.7
% Solids Vacuum Filter Cake	55.8	55.6

Bacteria samples collected before and during the plant trial showed no differences in either total coliform or standard plate count organism concentrations. Coliform bacteria were not detected before or during the trial in the Brennan Plant effluent. Standard plate count results varied in the plant effluent samples both before and during the plant trial with no apparent trends attributed to the plant trial.

Distribution system samples collected for THM analysis clearly revealed the effect of the increasing XE-392 dose (see Table 6) during the trial. THM concentrations increased with increasing distance from the Brennan Plant and decreased in samples influenced by the Brennan Plant as the XE-392 dose was increased.

The distribution system samples reflect a 50% dilution with water treated by the control clarifier. During the period when 18 mg/L of XE-392 was applied to the test clarifier, control clarifier THMFP was higher than test clarifier THMFP by a factor of 2.1. The following expression could therefore be used to predict the Brennan Plant Effluent THM concentration:

$$\frac{(1.0 + 2.1)}{2} \text{ Test Clarifier THM} = \text{Plant Effluent THM}$$

Using this equation, a value for the test clarifier can be derived based on the 95.6 ug/L THM recorded in the Brennan Plant effluent sample. This is necessary because plant effluent samples reported during this study were dechlorinated upon collection and reflect an unknown detention time.

Softener effluent THM samples reported reflect a 24 hour storage time with residual chlorine. Using the values from the table, a new series of expected THM values for the six sample points can be calculated using the predicted test clarifier THM value and the percent increase noted with increasing distance from the Brennan Plant. These numbers are expressed on the bottom of Table 6 and indicate that full scale use of the material for THM control will bring this system into compliance with the current THM MCL.

TABLE 6

INFLUENCE OF PLANT-SCALE TRIAL ON
DISTRIBUTION SYSTEM THM CONCENTRATION (µg/L)

XE-392 Dose In Use At Time Of Sampling, mg/L	SAMPLE SITE # (IN ORDER OF INCREASING DISTANCE FROM BRENNAN PLANT)							
	Brennan Plant	1	2	3	4	5	6	7
0 (Control)	141	-	157	152	173	272	254	265
3.8 (50% blend w/control softener)	120	134	183	186	185	194	239	280
12.0 (50% blend w/control)	109	132	156	160	155	208	232	250
16.0 (50% blend w/control)	106	129	141	139	144	214	207	233
18.0 (50% blend w/control)	95.6	130	145	144	156	168	206	286
18.0 (both softeners) (Estimated)	61.7	84	94	93	101	108	133	*

* Sample Site #7 influenced predominantly by Marion Street Plant - Reflects Distribution System background conditions and is not included in calculations for predicted THM.

SECTION 9

DISCUSSION OF COSTS

The experimental coagulant, XE-513, is expected to cost approximately $6.00 per pound when purchased in bulk. Current City of Daytona Beach total water plant operating costs for lime softening (including solids handling) are approximately 0.33 dollars per 1,000 gallons (February, 1984 costs). If the experimental coagulation process is used, the XE-513 cost is expected to be 0.38 dollars per 1,000 gallons, assuming a dose of 7.5 mg/L.

Based on the treatment of 0.53 m^3/s (12 MGD), an annual operating cost increase of $1.64 million is anticipated for the purchase of XE-513 alone. Operating costs for purchase of ferric sulfate (10 mg/L dose) and conventional polymer (1.0 mg/L dose), shown to be necessary in this study, will increase operating cost by an additional $0.04 per 1,000 gallons. It is assumed that no increase in solids handling cost will be associated with this process. Total operating cost increase using this process is estimated to be $0.42 per 1,000 gallons or $1.84 million per year at 12 MGD treated flow. Total water plant operating costs would therefore be $0.75 dollars per 1,000 gallons.

Capital costs for implementation of this process are expected to be minimal because major plant modifications would not be necessary. Equipment requirements are expected to include:

One XE-513 Storage Tank
Three XE-513 Metering Pumps
One Ferric Sulfate Storage Tank
Three Ferric Sulfate Metering Pumps
One Concrete Foundation/Dike/Housekeeping Slab Structure
Emergency Shower and Eyewash Station
Piping
Instrumentation

Estimated cost for these additions is $32,500 (1984 costs). Not included in the operating and capital costs outlined above, however, are additional sampling and analytical costs necessary for proper control of this process. Techniques for monitoring THMs via surrogate parameters (i.e., UV absorbance, turbidity, TOC, TOX monitors) have not, to date, been proven commercially. It is therefore assumed at this time, routine sampling and THM analyses would be necessary for process control.

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APPENDIX A

EXPERIMENTAL METHODS

ANALYSIS METHODS:

1. COLOR

   True, expanded low range apha platinum-cobalt stds. Reference 19, p. 60, 204.

2. TURBIDITY

   Reference 19, p. 132, 214A. Nephelometric method-NTU's. Instrument-ratio turbidimeter Hach model 18900.

3. HARDNESS

   Reference 19, p. 195, 314B. EDTA Titrimetric method.

4. CHLORINE RESIDUAL

   Reference 19, p. 289, 408D, DPD ferrous titrimetric method.

5. pH

   Reference 19, p. 402, 423 pH value.
   Instrument-Orion model 601A digital ionalyzer.

6. TRIHALOMETHANES:

   Reference 21, liquid/liquid extraction, method 501.2, instrument Hewlett-Packard 5840 gas chromatograph with electron capture detector. THMFP refers to sample chlorinated and stored for 24 hours at ambient temperature.

7. ALKALINITY

   Reference 19, 0. 253, 403 Alkalinity.

8. TOTAL ORGANIC CARBON (TOC) ANALYSIS:

   Reference 22, total organic carbon, method 415.1 Beckman Toca Master.

9. TOTAL ORGANIC HALOGENS (TOX) ANALYSIS:

   Method 450.1

10. IRON

    Reference 19, p. 199, 315.

11. ULTRAVIOLET ABSORBANCE (UV)*

UV absorbance was determined by the following methods:

a. The pH was adjusted to 4.0 using 1N HCL and 1N NaOH.
b. Samples were centrifuged for 3 minutes.
c. The UV absorbance was measured at 254 nm using the Bausch & Lomb 710 spectrophotometer.

*No standard methods currently exist for UV absorbance, the method used here is similar to the method used in several other THM precursor studies and therefore allows for direct comparison of this data with data developed in the other studies.

12. SETTLEABLE SOLIDS:

Reference 19, p. 96, 209F, 1 hour in a 1000 ml graduated cylinder.

13. TOTAL SOLIDS

Reference 19, p. 92, 209A.

14. VOLATILE SOLIDS

Reference 19, p. 95, 209E.

15. TOTAL COLIFORM

Reference 19, p. 806, 909A membrane filter technique.

16. STANDARD PLATE COUNT

Reference 19, p. 789, 907.

METHOD OF SAMPLE COLLECTION AND HANDLING FOR BOTH PILOT PLANT STUDY AND FULL SCALE STUDY

I. PROCESS CONTROL SAMPLES:

A. Samples for process control were analyzed immediately after collection making preservation techniques unnecessary. Samples in both the pilot plant and plant scale operations were collected by means of a polypropylene lab beaker fastened to a pole of sufficient length to permit easy dipping of samples from treatment process tanks or weirs. Care was taken to insure that the samples were representative of water quality in each tank sample. Where samples were collected from a weir, said samples were taken from the junction point exiting the weir. Samples were taken at least two inches below the surface to avoid inclusion of surface films. Process control parameters monitored included:

1. pH
2. Alkalinity
3. Chlorine Residual
4. Turbidity
5. Hardness
6. Color
7. Solids

B. Iron samples, if not analyzed immediately upon collection, were preserved using nitric acid and stored at 4°C.

II. SAMPLES FOR ORGANICS ANALYSIS:

A. Samples for trihalomethane analysis were collected in 3 oz. amber glass bottles and sealed by means of screw caps with teflon-faced silicone liners. The teflon face of the cap liner was the side in contact with the water sample. Samples were collected from free flowing taps. Instantaneous trihalomethane samples were dechlorinated immediately upon collection using 2.5 to 3 mg of sodium thiosulfate per 40 ml. sample and stored at 4°C. Unchlorinated samples analyzed for THM formation potential were chlorinated at various doses using the Brennan Plant process chlorine feed solution. The chlorine residual was checked after the formation period to verify the presence of a free chlorine residual.

B. Total organic halogen samples were collected in 500 ml. amber glass bottles and sealed by means of screwcaps with teflon-faced

silicone liners. The teflon face of the cap liner was the side in contact with the water sample. The clarifier effluent samples were chlorinated using dosage of 35 mg/L and then stored at ambient temperature for 24 hours. After 24 hours, the samples were dechlorinated using sodium sulfite and stored at 4°C until shipping to the EPA Municipal Environmental Research Laboratory in Cincinnati, Ohio.

C. Total organic carbon samples were collected in 2 ounce glass bottles provided by a local commercial laboratory. The bottles were sealed by means of screw cap with teflon faced liners with the teflon faced side in contact with the sample. Samples were preserved by reducing the pH to less than 2 using HCL. Samples were stored at 4°C and analyzed by the commercial lab.

D. Ultraviolet absorbance samples taken during the pilot plant study were analyzed by a commercial lab. Samples were collected in 2 ounce glass bottles and sealed by means of screw caps with teflon faced liners. The teflon faced side of the liners were the sides in contact with the water sample. Samples were stored at 4° C and analyzed within 24 hours. Any samples held over 24 hours were frozen until time of analysis.

UV absorbance samples collected during the full scale study were collected in 3 oz. amber glass bottles. The bottles were sealed by means of screw caps with teflon-faced silicone liners. The teflon-faced side of the liner was the side in contact with the sample. Samples were analyzed in the Ralph F. Brennan Water Plant Laboratory during the full scale study. The absorbance samples which were not immediately analyzed were frozen until actual time of analysis.

III. SAMPLES FOR BACTERIOLOGICAL ANALYSIS:

A. These samples were analyzed for total coliform bacteria and standard plate count organisms. All samples were collected from free flowing taps using pre-sterilized plastic Whirl-Pak - Nasco Co., containers. Chlorinated samples were collected in similar containers which contained 10 mg of sodium thiosulfate. Samples were stored at 4° C and were analyzed within six hours.

IV. RECORDS:

A. All sample containers were labeled upon sample collection with the following: date, time of collection, sampling point, collector's initials, analysis to be performed and other pertinent information (i.e., chlorine residual, quenched or unquenched, pH). Sample ID Numbers were assigned as the samples were received in the laboratory, and were added to the label.

TABLE A-1

SUMMARY OF SAMPLE HANDLING TECHNIQUES

FOR ORGANIC ANALYSES

PARAMETER	PRESERVATIVE	CONTAINER	MAX. HOLDING TIME
Trihalomethanes	Cool, 4°C	Glass, Teflon-lined septum	14 days
Total Organic Carbon	Cool, 4°C HCl to pH 2	Glass, Teflon-lined septum	28 days
UV Absorbance*	Cool, 4°C HCl to pH 4	Glass, Teflon-lined septum	14 days

* No standard holding times and preservation techniques known by authors.

TABLE A-2

SUMMARY OF SAMPLING LOCATIONS

PILOT PLANT	RALPH F. BRENNAN WATER PLANT	DISTRIBUTION SYSTEM
Raw water influent line	Raw water influent line	Regional Wastewater Plant
#1 floc tank	#1 clarifier effluent	Shell Station at Intersection of I-95 and U.S. 92
Clarifier effluent	#2 clarifier effluent	Indigo Inn
Filter effluent	#1 clarifier sludge withdrawal line	Airport Terminal
Plant effluent	#2 clarifier sludge withdrawal line	Derbyshire Fire Station
	Sludge thickener tank	Shady Place
	Vacuum filter	Pelican Bay Club House
	Washwater recovery basin	3011 N. Halifax
	Clearwell	
	Plant effluent	

TABLE A-3

ANALYSES PERFORMED DURING PILOT PLANT STUDY

PARAMETER MEASURED	SAMPLE LOCATION	MONITORING FREQUENCY
1. COLOR:		
	Raw	Daily
	Clarifier effluent	Daily
	Plant effluent	Daily
2. TURBIDITY:		
	Raw	Daily
	Clarifier effluent	Daily
	Plant effluent	Daily
3. HARDNESS:		
	Raw	Daily
	Plant effluent	Daily
4. CHLORINE RESIDUAL:		
	Raw (24 hour THMFP)	Daily
	Filter effluent (24 hour THMFP)	Daily
	Filter effluent (7 day THMFP)	Once
	Plant effluent	Hourly
	Plant effluent (24 hour THMFP)	Daily
	Raw	Daily
	#1 floc tank	Hourly (for plant process control)
	Clarifier effluent	Daily
	Plant effluent	Hourly
6. TRIHALOMETHANE:		
A. Initial Trihalomethane:		
	Raw	Daily
	Filter effluent	Once
	Plant effluent	Daily
B. 24 Hour Trihalomethane Formation Potential:		
	Raw	Daily
	Filter effluent	Twice
	Plant effluent	Daily

TABLE A-3 (continued)

PARAMETER MEASURED	SAMPLE LOCATION	MONITORING FREQUENCY
C. Seven day Trihalomethane Formation Curve:	Raw	Twice
	Filter effluent	Once
D. GC/MS:	Raw	Once
	Plant effluent	Once
7. ALKALINITY:	Raw	Daily
	Clarifier effluent	Daily
	Plant effluent	Daily
8. TOTAL ORGANIC CARBON:	Raw	Daily
	Plant effluent	Daily
9. IRON:	Raw	Once
	Plant effluent	Daily
10. UV ABSORBANCE (254mm):	Raw	Daily
	Filter effluent	Daily

TABLE A-4

ANALYSES PERFORMED DURING FULL SCALE STUDY

	PARAMETER MEASURED	SAMPLE LOCATION	MONITORING FREQUENCY
1.	COLOR:		
		Raw	Daily
		#1 clarifier effluent	Twice Daily
		#2 clarifier effluent	Twice Daily
		Plant effluent	Twice Daily
2.	TURBIDITY:		
		Raw	Daily
		#1 clarifier effluent	Twice Daily
		#2 clarifier effluent	Twide Daily
		Plant effluent	Twice Daily
3.	HARDNESS:		
		Raw	Daily
		Plant effluent	Daily
4.	CHLORINE RESIDUAL:		
		Raw (24 Hour THMFP)	Daily
		#1 clarifier effluent (24 hour THMFP)	Twice Daily
		#2 clarifier effluent (24 hour THMFP)	Twice Daily
		Plant effluent	Daily
		Plant effluent (24 hour THMFP)	Twice Daily
		1 mg/L L650E solution (24 hour THMFP)	Once
		Wash Water Recovery	Once
		Raw (7 day formation curve)	Twice
		Plant effluent formation curve	Once
5.	pH:		
		Raw	Daily
		#1 clarifier effluent	Twice Daily
		#2 clarifier effluent	Twice Daily
		Plant effluent	Twice Daily
6.	TRIHALOMETHANE:		
	A. Initial Trihalomethane	Raw	Daily
		Plant effluent	Daily
		Distribution System	Weekly

TABLE A-4 (continued)

PARAMETER MEASURED	SAMPLE LOCATION	MONITORING FREQUENCY
B. 24-Hour Trihalomethane Formation Potential Curve	Raw	Daily
	#1 clarifier effluent	Twice Daily
	#2 clarifier effluent	Twice Daily
	Plant effluent	Twice Daily
	1 mg/L L650E Solution	Once
C. Four-Day Trihalomethane Formation Potential Curve	#1 clarifier effluent	Once (during optimum conditions)
	#2 clarifier effluent	Once (during optimum conditions)
D. Seven-Day Trihalomethane Formation Curve	Raw	Twice
E. GC/MS	Raw	Once
	#1 clarifier effluent	Once (during optimum conditions)
	#2 clarifier effluent	Once (during optimum conditions)
7. ALKALINITY:	Raw	Daily
	#1 clarifier effluent	Twice Daily
	#2 clarifier effluent	Twice Daily
	Plant effluent	Twice Daily
8. TOTAL ORGANIC CARBON:	#1 clarifier effluent	Daily
	#2 clarifier effluent	Daily
	Plant effluent	Daily
9. TOTAL ORGANIC HALOGENS:	#1 clarifier effluent	Daily
	#2 clarifier effluent	Daily
10. IRON:	Raw	Daily
	#1 clarifier effluent	Daily
	#2 clarifier effluent	Daily
	Plant effluent	Daily
11. UV ABSORBANCE (254 nm):	Raw	Daily
	#1 clarifier effluent	Daily
	#2 clarifier effluent	Daily

TABLE A-4 (continued)

	PARAMETER MEASURED	SAMPLE LOCATION	MONITORING FREQUENCY
12.	SETTABLE SOLIDS:	#1 clarifier effluent	Daily
		#2 clarifier effluent	Daily
13.	TOTAL SOLIDS:	#1 clarifier sludge	Daily
		#2 clarifier sludge	Daily
		Filter feed to vacuum filter	Daily
		Filter cake from vacuum filter	Daily
14.	TOTAL VOLATILE SOLIDS:	#1 clarifier sludge	Daily
		#2 clarifier sludge	Daily
15.	TOTAL COLIFORM:	Raw	Daily
		Plant effluent	Daily
16.	STANDARD PLATE COUNT:	Raw	Daily
		Plant effluent	Daily

APPENDIX B

QUALITY ASSURANCE REPORTS

Three quality assurance reports were developed during the course of this investigation. The methodologies used in the preparation of these reports is discussed and the three reports are reproduced in this Appendix.

PRECISION

Duplicates were analyzed daily or a minimum of every 10 samples for each parameter. Documentation involved tables of mean, standard deviation, and relative standard deviation. Quality control limits were defined using relative standard deviation (rsd). Twice rsd determines the warning limit and 3 times rsd sets the control limit. Study objectives were met with respect to alkalinity, hardness, pH, chloroform, bromdichloromethane, dibromchloromethane, bromoform, and total trihalomethanes.

The use of relative standard deviation to set control limits for color, chlorine, and turbidity proved to be inadequate. Considering the limitations inherent in the analytical method and the low level concentrations being tested a more reliable statistical approach is to use standard deviations for concentrations in a limited range.

ACCURACY

The quality assurance program dictated that a performance sample for each desired paramter be analyzed once during the study. EPA Quality Assurance samples were analyzed for the following parameters: turbidity, pH, alkalinity, calcium, magnesium, chloride, total hardness, chloroform, bromdichloromethane, dibromochloromethane, bromoform, total trihalomethanes, and iron. All results were acceptable. During the course of this study EPA performance samples for state lab certification were analyzed for trihalomethanes, turbidity, chlorine, and fluoride.

Standard curves for color, iron and trihalomethanes were constructed and verified routinely. Values fell within 10% for color and iron, 20% for trihalomethanes.

No problems occurred with blank values for trihalomethane analyses. All values were less than 10 µg/L total trihalomethanes.

QUALITY CONTROL CHECKS/CORRECTIVE ACTION TAKEN

1. During jar testing a dibromochloromethane standard did not fall within 20% of its known value. A second standard was prepared, resulting in a 99.8% accuracy.

2. Between the full scale trial and pilot plant run #2 the Hach DR_2 spectrophotometer for color analyses malfunctioned. A distilled water blank could not be adjusted to 100% transmittance. Routine instrument checks did not correct or reveal the problem. The instrument was sent off for repairs and returned before pilot plant run #2. A new standard curve was constructed prior to pilot plant run #2.

MAINTENANCE

No major maintenance was required throughout the study. Minor problems centered around the chemical feed systems in both pilot plant and full scale trials. A daily calibration program helped to diagnose and correct chemical dose problems quickly.

DATA REDUCTION AND VALIDATION

All analytical data passing quality assurance and control checks was considered valid and incorporated into the final report.

As a result of quality assurance checks data was rejected for the following reasons:

1. Trihalomethane analyses: sample did not have a measurable free chlorine residual.

2. Twenty-four hour THMFP: sample held longer than 24 hours before dechlorination.

QUALITY ASSURANCE REPORT ON PHASE I TRIHALOMETHANE STUDY

Precision:

Duplicates were run on at least every ten samples resulting in one duplicate set per set of jar tests. Mean, standard deviation, and relative standard deviation were calculated for chloroform, bromodichloromethane, dibromochloromethane, bromoform and total trihalomethanes (see attachment). All duplicates fell within the control limits for precision as developed for this study.

Accuracy:

1. Standards for checking standard curve: Standards were run at the beginning and end of each sample set. Area amount from these standards are compared to the working standard curve and percent accuracies are calculated. Study objectives require ± 20% accuracy. All standards with the exception of dibromochloromethane on June 21, 1983, fell within ± 20% (see troubleshooting for details).

Average percent accuracy and percent accuracy range for each parameter were as follows:

	$CHCL_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
average	96.2	99.0	103	101	98.6 average
range	89.7-102	87.7-105	87-117	84-108	85-108 range

2. Performance samples: EPA performance samples were analyzed for pH, calcium, total hardness, total alkalinity, and turbidity. All samples provide to be within acceptable accuracy limits with the exception of concentrate #2 alkalinity and hardness, which was spiked with a potable water sample (see attachment).

Blank Values:

Each sample set contained a chlorinated blank which was stored with the sample set, dechlorinated and analyzed for Trihalomethanes. Average blank value was 1.3 µg/L. Values ranged from 1.0 - 6.4 µg/L. A geometric average was calculated due to the 6.4 µg/L results. Most values ranged from 1.0 - 1.3 µg/L.

Troubleshooting:

G.C. septa were changed 6/20, 7/1, 7/14, and 7/29 when retention times started to drift.

On 7/15 argon/methane gas cylinders were changed. For preventive maintenance the Electron Capture Detector temperature was raised to 350°C to provide thermal conditioning in case of contamination from change-over.

On 7/26 all G.C. temperature systems were down to preset values due to a thunderstorm. All systems were put through thermal conditioning on July 28, prior to any additional analyses. On July 29, standards were falling just within ±20 percent. A new standard curve was constructed as the column lost sensitivity during the prolonged downtime.

On June 21, 1983, the standard for dibromochloromethane did not fall within the ±20 percent limit. This proved to be attributable to a bad Supelco standard. An in-house standard gave a percent accuracy of 99.8%.

E.P.A. Performance Samples

PARAMETER	SAMPLE	OBSERVED VALUE (µg/L)	TRUE VALUE (µg/L)	PERFORMANCE STUDY 95% CONFIDENCE LIMITS	% ACC.	PROJECT OBJECTIVES
pH	Conc. 1	5.7	5.7	5.58-5.82	100	±0.1
pH	Conc. 2	7.8	7.8	7.64-7.96	100	±0.1
Calcium	Conc. 1	42	40.6	35.9-44.5	103	---
Calcium	Conc. 2	4.8	5.3	4.52-6.12	91	---
Tot. Hardness	Conc. 1	135	136	127 - 142	99	±5 %
Tot. Hardness	Conc. 2	16	20.7	16.5-24.4	77	±5 %
Tot. Alkalinity	Conc. 1	74	74.7	69.3-77.5	99	±5 %
Tot. Alkalinity	Conc. 2	17	21.7	18.7-24.9	78	±5 %
Turbidity	Conc. 1	4.2	4.27	----	98	±5 %
Turbidity	Conc. 2	.84	.82	----	102	±5 %

H. Zwart-Duryea,
Chemist
08/83

Precision Data - Phase I

Chloroform

Study Objective: relative standard deviation 3.0%
warning limit 6.0%
action limit 9.0%

Result (µg/L)	Duplicate (µg/L)	Mean (µg/L)	S (µg/L)	rel. S (%)
328.	322.	325.	3.54	1.09
316.	311.	314.	3.75	1.20
191.	199.	195.	5.30	2.72
230.	230.	230.	.141	.0614
141.	147.	144.	4.24	2.94
92.	94.	93.	1.48	1.59
140.	139.	140.	.778	.557
312.	315.	314.	1.84	.586
77.0	74.4	75.7	1.84	2.43
286.	295.	291	6.36	2.19
65.3	68.0	66.7	1.91	2.86
66.6	66.4	66.5	.141	.212
64.7	62.7	63.7	1.41	2.21

H. Zwart-Duryea
08/83

Precision Data - Phase I

Bromodichloromethane

Study Objective: relative standard deviation 4.24%
warning limit 8.48%
action limit 12.72%

Result (µg/L)	Duplicate (µg/L)	Mean (µg/L)	S (µg/L)	Rel. S (%)
78.0	76.4	77.2	1.13	1.46
57.6	56.3	57.0	.919	1.61
39.0	41.0	40.	1.41	3.53
36.9	37.0	37.	.0707	.191
51.0	51.9	51.4	.636	1.24
34.5	34.7	34.6	.141	.408
33.1	33.9	33.5	.566	1.69
28.3	26.9	27.6	.990	3.59
30.6	31.9	31.2	.919	2.94
27.1	27.1	27.1		
36.6	35.5	36.0	.778	2.16
25.5	26.7	26.1	.848	3.25

H. Zwart-Duryea,
08/83

Precision Data - Phase I

Dibromochloromethane

Study Objective: relative standard deviation 2.22%
warning limit 4.44%
action limit 6.66%

Result (µg/L)	Duplicate (µg/L)	Mean (µg/L)	S (µg/L)	Rel. S (%)
21.1	20.7	20.9	.283	1.35
11.2	11.0	11.1	.141	1.27
11.7	12.3	12.0	.424	3.53
8.3	8.3	8.3	0	0
24.8	25.1	25.	.212	.850
11.2	11.2	11.2	0	0
3.0	3.1	3.0	.0707	2.36
13.8	13.1	13.4	.495	3.69
2.8	2.9	2.8	.0707	2.52
13.3	13.4	13.4	.0707	.530
24.1	23.4	23.8	.495	2.08
11.3	11.7	11.5	.283	2.46

H. Zwart-Duryea,
09/83

Precision Data - Phase I

Bromoform

Study Objective:	relative standard deviation	11 %
	warning limit	22 %
	action limit	33 %

Result (µg/L)	Duplicate (µg/L)	Mean (µg/L)	S (µg/L)	Rel. S (µg/L)
3.0	2.9	3.0	.0707	2.40
1.3	1.4	1.4	.0707	5.05
2.2	2.3	2.2	.0707	3.21
1.0	1.0	1.0	0	0
.8	.8	.8	0	0

H. Zwart-Duryea,
08/83

Precision Data - Phase I

Total Trihalomethanes

Study Objective: relative standard deviation 1.33%
warning limit 2.66%
action limit 3.99%

Result (µg/L)	Duplicate (µg/L)	Mean (µg/L)	S (µg/L)	Rel. S (%)
427	420	424	4.95	1.17
385	378	382	4.95	1.30
242	252	247	7.07	2.86
275	275	275	0	0
171	174	172	2.26	1.31
186	185	186	.707	.381
348	352	350	2.12	.607
120	116	118	1.41	1.18
320	330	325	7.07	2.18
108	108	108	0	0
128	124	126	2.83	2.24
103	107	105	2.83	2.70

H. Zwart-Duryea,
08/83

QUALITY ASSURANCE REPORT ON PHASE II TRIHALOMETHANE STUDY

Precision:

Duplicates were run daily on each parameter resulting in at least one duplicate for every 10 samples analyzed. Mean, standard deviation, and relative standard deviation were calculated for each set of duplicates. Values were compared to study objectives and established control limits. The following table represents the precision data from Phase II - Pilot Plant Study:

Parameter	Study Objective	Control Limit	Avg. Rel. Std. Dev.	# Analyses Outside Control Limit
Alkalinity	2.0 % rsd	6.0 % rsd	0.392%	none
Chlorine	0.3 % rsd	0.9 % rsd	0.10 %	1
Color	3.6 % rsd	9.8 % rsd	3.79 %	1
Hardness	3.6 % rsd	9.8 % rsd	0.55 %	none
pH	±0.5 pH	±0.15 pH	0.00 %	none
Turbidity	3.9 % rsd	11.7 % rsd	5.53 %	2
Chloroform	3.00 rsd	9.00 rsd	1.68 %	none
Bromodi-chloromethane	4.24% rsd	12.72% rsd	2.34 %	none
Dibromo-chloromethane	2.22% rsd	6.66% rsd	1.97 %	none
Bromoform	11.0 % rsd	33.00% rsd	.608%	none
Total Tri-halomethane	----	----	1.81 %	----

Troubleshooting:

Chlorine: The single analysis resulting in a 1.9% relative standard deviation represents duplicate analysis of 3.8 mg/L and 3.7 mg/L. Most of the time duplicate chlorine analyses result in 0.0 mg/L standard deviation. A difference of only 0.1 mg/L therefore falls outside the present control limit. This is less than a 5% difference in values.

Color: The slope on the color curve at low values, i.e., less than 5 cu., is quite sharp. In the case of 29.8% relative standard deviation, the percent transmittance values were 98% and 97% for the duplicate set, resulting in final results of 1.5 cu. and 2.3 cu., respectively. The transmittance scale reflects only a 1% difference in transmittance values.

Turbidity: Two duplicate sample sets during the pilot plant study exceeded the control limit. Duplicate results for both sets were .09 NTU and .11 NTU with a calculated standard deviation of .014 and relative standard deviation of 14%.

In each of the above analyses, a problem occurs when analyzing at extremely low concentrations. Any deviation in duplicate results at low concentrations creates an out of control situation when the control limits are set from relative standard deviations calculated from a wide range of concentrations. While this data is believed valid, a different warning and control limit calculated for low range values might be more appropriate. Relative standard deviations were chosen for control limits to avoid creating different limits for varying concentrations. For the most part this work very well, with the exception of very low concentrations in relation to the average concentrations analyzed in the laboratory.

Accuracy:

Trihalomethanes: City-laboratory-prepared THM standards or purchased Supelco THM standards were run at the beginning and end of each analysis day. Area amounts are compared to the working standard curve and percent accuracies are calculated. Study objectives require a ± 20% accuracy. The following table represents the average percent accuracy and percent accuracy range for trihalomethane analysis during Phase II - Pilot Plant Study.

Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform	TOTAL THM
98.3%	102%	102%	104%	102%
91-104%	96-110%	96-112%	96-117%	97-110%

Color: On August 4, color standards were prepared from a stock 500 cu standard APHA-Hazen to verify the Hach card scale for color readings. The following table represents values from Hach color card and true values.

True Value (CU)	5	10	25	50	100
Observed Value (Hach Card (CU))	5	8	23	47	98

Due to the differences, a card representing percent transmittance is now being used in the color analysis. Transmittance values are compared to a standard curve representing transmittance vs. color units.

Iron: On August 24, the table used to translate percent transmittance to mg/L iron was checked using a 1000 mg/L iron standard. True values and observed values were as follows:

True Value	.05 mg/L	.3 mg/L	.1 mg/L	.5 mg/L	.8 mg/L
Observed Value	.03 mg/L	.3 mg/L	.1 mg/L	.4 mg/L	.7 mg/L

The differences obtained were probably due to the diluting of a 1000 mg/L standard down to such low values. To verify the technique and analytical procedures were accurate, EPA performance samples were analyzed with the following results:

	True Value	Obs. Value	% Accuracy
Concentrate #4	.02 mg/L	.02 mg/L	100
Concentrate #5	.08 mg/L	.09 mg/L	112
Concentrate #6	.9 mg/L	.89 mg/L	99

Blank Values: Each sample set for trihalomethane analysis included a blank of organic free water subjected to the same conditions as the collected samples and analyzed for THMs. The average blank value was 1.6 µg/L. Values ranged from 0 to 18.3 µg/L. Because of the 18.3 µg/L blank, a geometric average was calculated as all other values ranged from 0.0 to 2.8 µg/L.

Maintenance:

Gas Chromatograph: Injection port septa were changed on August 12 and August 20.

Pilot Plant: All rotameters were checked at the beginning of the pilot study to verify flows accuracy. Chemical feed pumps were checked daily to insure proper dosages. Filters were backwashed when the flow could not be adjusted to 9.6 lpm. Backwashing took place on the following dates: 8/10, 8/14, 8/18, 8/22, and 8/26.

The line delivering the 1 percent polymer solution became plugged on three occasions requiring a flushing of the line.

The lime recirculation pump required impeller replacement due to the abrasive action of the lime slurry.

The ferric sulfate pump stopped feeding at one point. The poppet value and O-rings had become encrusted with iron deposits, and had to be cleaned.

Conclusions: Quality Assurance and Quality Control objectives were maintained during Phase II - Pilot Plant Study. A problem persisted in meeting the precision limits for chlorine, color, and turbidity when working with low concentrations relative to the average concentration used to set the limits. For future work, new limits should be established for low concentrations when sufficient data has been collected.

QUALITY ASSURANCE REPORT ON PHASE III TRIHALOMETHANE STUDY

Precision: Duplicates were run daily on each parameter resulting in at least one duplicate for every 10 samples analyzed. Standard deviation and relative standard deviations were calculated and compared to quality control limits. The following table represents precision data for Phase III - Full Scale Trial.

Parameter	Study Objective (RSD)%	Control Limit (RSD)%	Phase III Avg. RSD	Analyses Outside Control Limit
Alkalinity	2.0	6.0	.57	none
Chlorine	0.3	0.9	.523	six
Color	3.6	9.8	3.22	one
Hardness	3.6	9.8	.656	none
pH	± 0.05 pH units	± 0.15 pH units	.218	none
Turbidity	3.9	11.7	3.02	two
Chloroform	3.00	9.00	1.38	none
Bromodichloromethane	4.24	12.74	1.66	none
Dibromochloromethane	2.22	6.66	1.36	none
Bromoform	11.0	33.0	4.51	none
Total THM	1.33	3.99	1.41	one

Troubleshooting:

Precision objectives were met for all parameters with the exception of chlorine. As mentioned in the quality assurance report Phase II, a 0.1 mg/L difference in chlorine results falls outside the quality control limit. With respect to chlorine analyses, a better quality control method of standard deviation of ±0.1 mg/L is recommended.

Accuracy:

Trihalomethanes: Standards were analyzed at the beginning and end of each day. Study objectives dictated results be within 20% of the known value. The following table represents accuracy data for trihalomethane analysis:

	Chloroform	Bromodi-chloromethane	Dibromo-chloromethane	Bromoform	Total THM
Average	97.7	101	102	102	99.8
Range	89.7-116	93.7-109	96.8-109	94.7-106	99.5-107

Blank Values:

A laboratory distilled water blank accompanied each sample set from collection point to analysis. Values ranged from 0.0 µg/L to 8.9 µg/L THM. Average value for Phase III was 1.0 µg/L THM.

Performance Samples:

EPA performance samples were analyzed for trihalomethanes on October 13, 1983. Results were acceptable.

Maintenance:

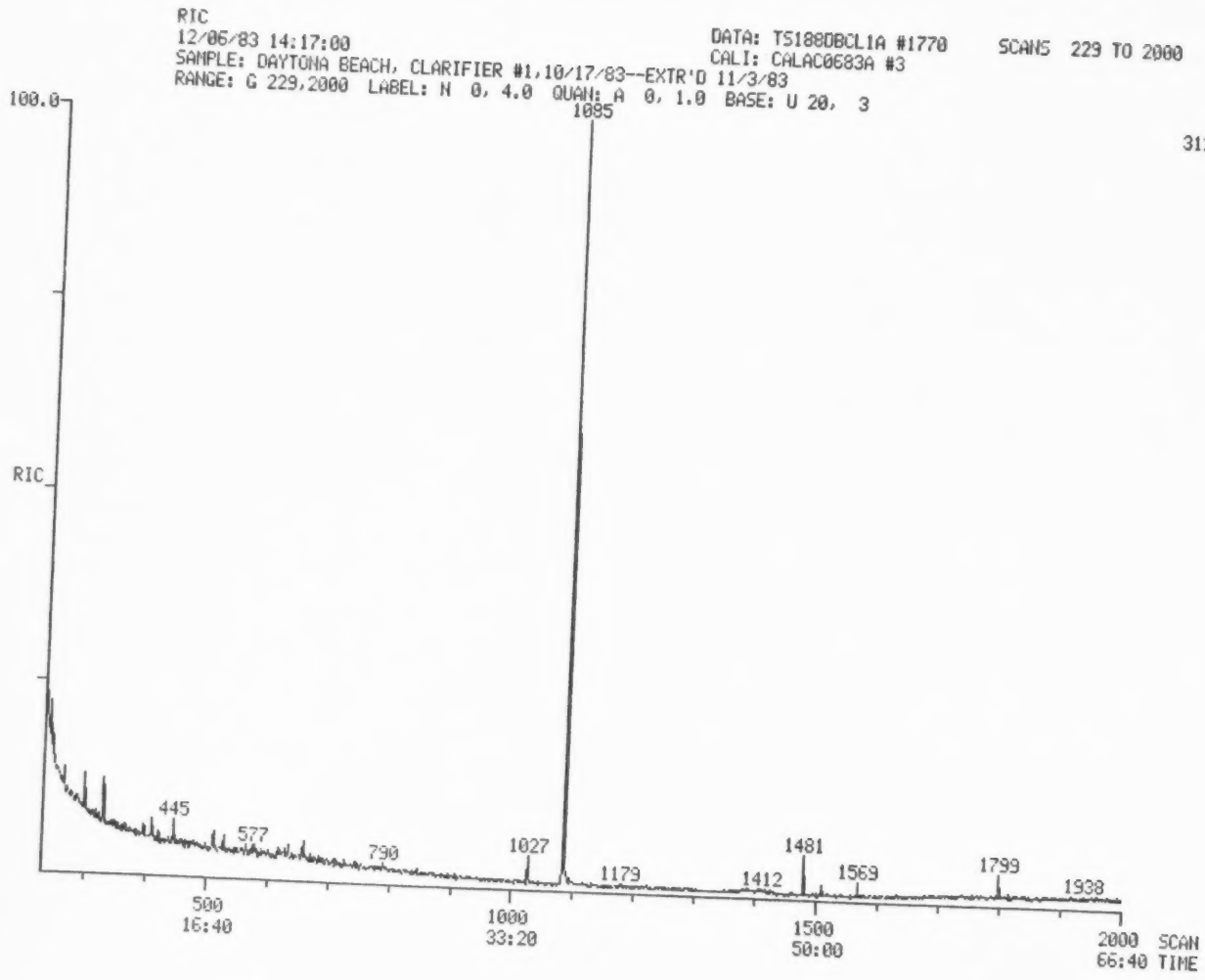
Gas Chromotograph: Injection port septa were changed every 2 weeks.

Brennan Plant: Raw water, plant effluent and filter flow gauges were calibrated prior to the full-scale study. These gauges were checked for accuracy every 3 months. Chemical feed pumps were checked daily to verify proper dosages. Filters at the Brennan Plant are backwashed every 100 hours. Excessive "air binding" during the initial stages of the study reduced run times to 72 hours. This was attributable to the point of chlorination being changed from pre-filtration to post filtration. Reverting back to pre-filtration chlorination restored filter run lengths to pre-study levels.

The polymer feed system required attention on several occasions. Problems in pumping occurred due to air in lines, inoperative check valves, and plugged polymer feed lines.

Conclusions:

Quality Assurance and Quality Control Objectives were maintained during Phase III - Full Scale Study. Minor maintenance problems were quickly discovered through daily calibrations of feed pumps and instrumentation, and promptly corrected.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DATA: TS188DBCL1A #1770
CALI: CALAC0683A #3
SCANS 229 TO 2000
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31264
445
577
790
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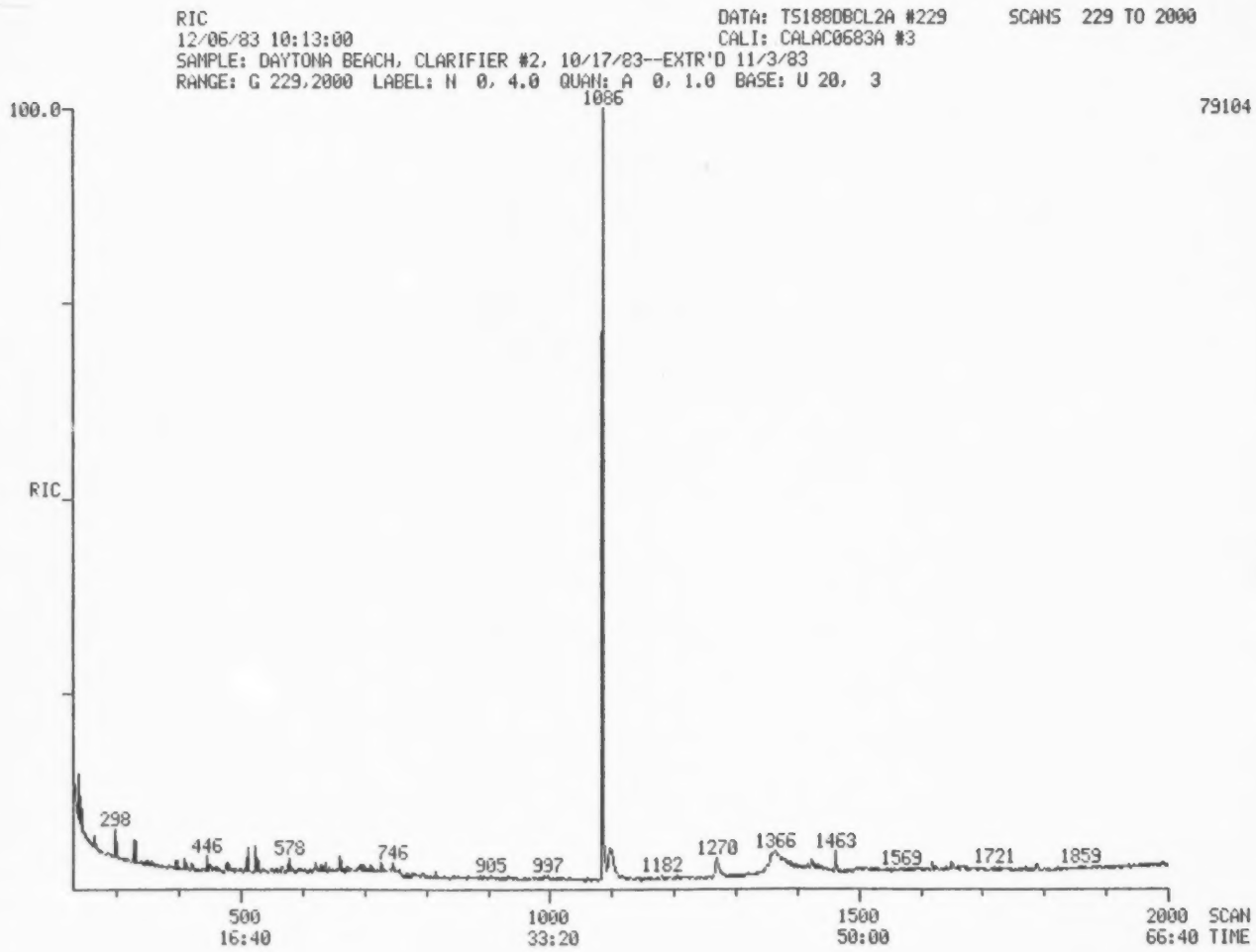
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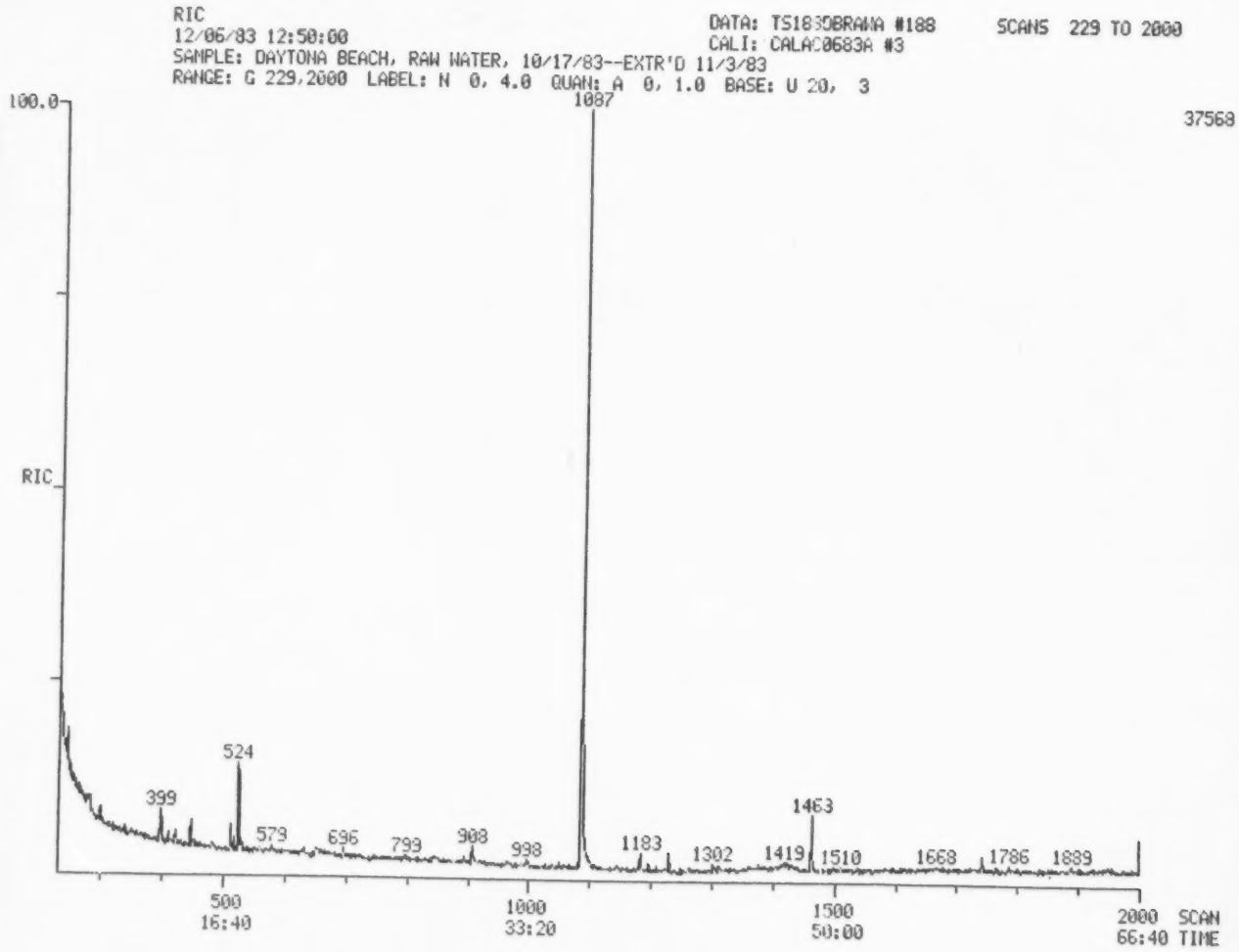
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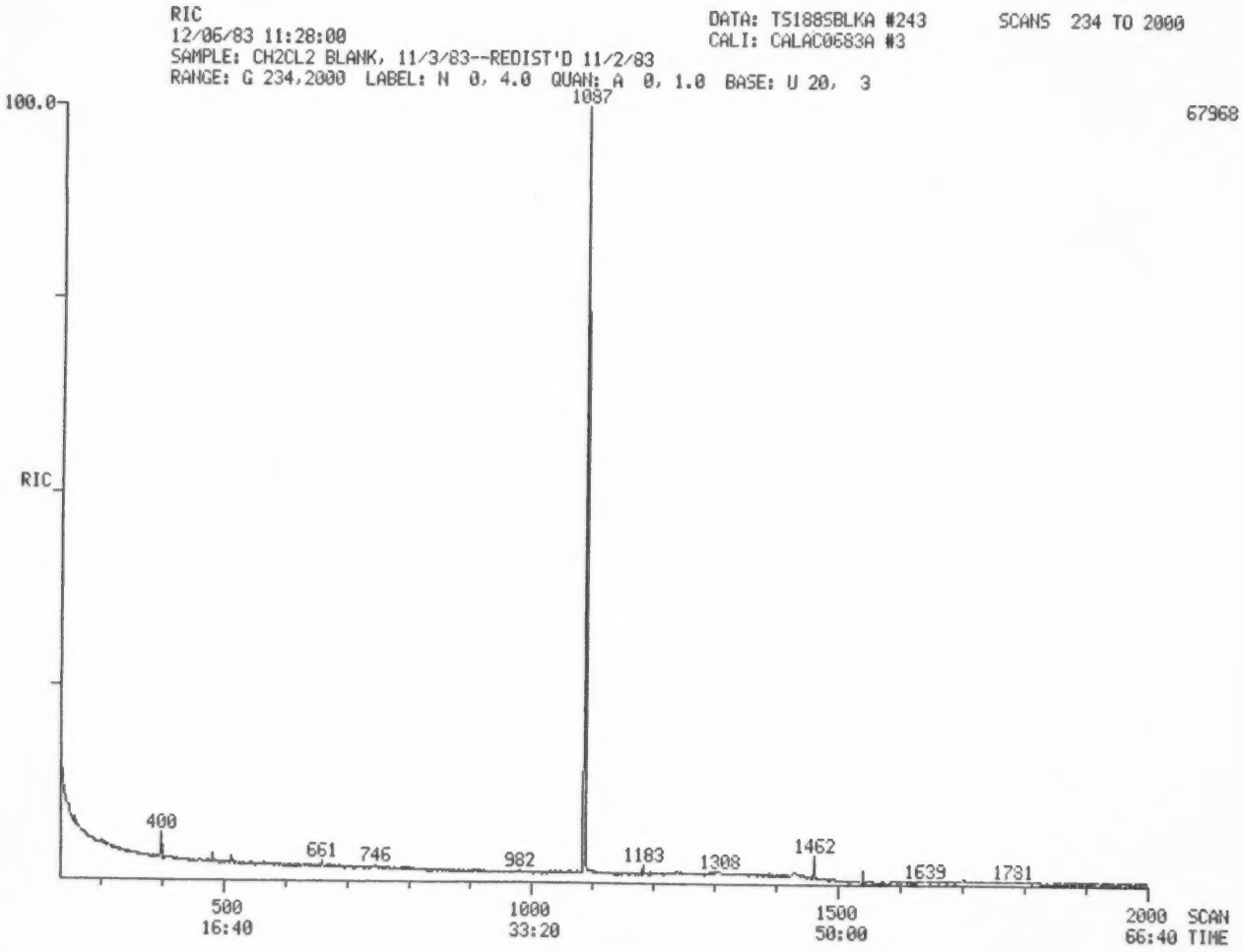
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APPENDIX C

JAR TEST PROCEDURE

GENERAL COMMENTS

Mix Time

Brennan Plant conditions indicate approximately 1.25 minutes rapid mix and 13.6 minutes slow mix time. Mixing in jar tests allowed for a rapid mix at 100 rpm for 1-2 minutes for each chemical addition and 15 minutes of slow mix at 50 rpm.

Lime Addition

Various methods of lime dosing were explored. Lime obtained from Brennan Plant lime silos was added directly to the jar in pre-determined doses in the beginning jar tests. This was not entirely satisfactory. The 200 mg/L dose used in the Brennan Plant was not adequate to create the desired pH 9.3 in the jar tests and some difficulty was experienced in obtaining consistent and reproducible pH values for a given lime dose. Adding sodium hydroxide or using a 440 mg/L lime does was often necessary to obtain the desired pH 9.3.

In an attempt to simulate the slaked lime feed system in the plant, a 20% W/V lime solution was prepared and added to the jars. It was found that approximately 2 mg/L added to 2 L of raw water would result in a pH 9.3. The reaction took approximately 2 minutes and then stabilized until the next chemical addition and provided adequate softening. This then became the method of lime addition for further jar tests. Results were consistent and reproducible.

Chemical Addition

Solutions were made fresh for each set of jar tests. Disposable polyethylene syringes were used to deliver the desired dose. The syringes allowed for quick dosing and rinsing to assure accurate deliveries.

Chlorine Addition

A chlorine solution from the Brennan Plant's chlorine feed system was used for chlorine dosing. The solution was tested daily using the DPD/FAS titration to determine mg/L chlorine.

GENERAL PROCEDURE

The following procedure was generally used for jar testing throughout this study.

1. Prepare necessary solutions.
2. Fill square plexiglass jars with 2000 ml. of raw water.
3. Set mixer to rapid mix speed - 100 rpm.
4. Add chemicals in desired order allowing approximately 1-2 minutes rapid mix per chemical addition.
5. Slow mix at 50 rpm for 15 minutes.
6. Settle for 10 minutes.
7. Siphon samples at least 2 inches below liquid surface.
8. Filter (Whatman #1 or .45 um membranes, depending on analyses).
9. Chlorinate.
10. Adjust pH to 8.0-8.5 with NaOH or HCl (as required).
11. Proceed with desired analyses or storage procedures.

Accompanying each jar set were a chlorinated organic free water blank and chlorinated raw water. These samples were handled the same as the treated water samples.

APPENDIX D

PILOT PLANT DESCRIPTION

The U. S. Environmental Protection Agency Mobile Pilot Water Treatment Plant consists of two identical water treatment systems installed in a 12.8 m long trailer. The plant is fabricated of stainless steel. The design critieria for each unit are:

Discharge:	Q = .32 lps
Rapid Mix:	1 - 2 minutes
Flocculation:	30 - 60 minutes
Settling:	3 - 6 hours
Filtration Flow Rate:	0.5 lps/ft^2

The plant has been designed for the following treatment processes: chemical coagulation and flocculation, sedimentation, filtration, and disinfection.

Because the plant consists of two hydraulically separate treatment plants, two simultaneous tests can be run or the units can be run in series to test the effect of 2-stage treatment methods. During this study, however, only one treatment plant was used.

Raw water is pumped from the raw water source into the constant head tank. Two stainless steel centrifugal pumps transfers water from the constant head tank to the rapid mix tank through valves and flow meters for flow adjustment.

The rapid mix tank of each system is a 37.8 L cylindrical tank 0.38 m in diameter and .46 m high. The water discharges from the rapid mix through a 2.54 cm diameter pipe. The mixer drive for each rapid mix is a D.C. variable speed Bodine fractional gear motor.

The flocculation tank was designed to provide gentle stirring to a flow of .32 liters per second with a 40 minute detention time. The 0.9 m square and 1.1 m high flocculation tank provides a water depth of .9m. The total waste volume is 0.76 M^3 or 27 $ft.^3$. The tank is divided into four chambers, each with its own variable speed mechanical mixer, allowing for tapered flocculation. The water exits the flocculation tank through a 2.54 cm diameter pipe.

The clarifier is 3 m long, 1.2 m wide, and 1.7 m high. With a water depth of 1.4 m and a flow rate of .32 lps the detention time is 4.4 hours.

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The clarifier is 3 m long, 1.2 m wide, and 1.7 m high. With a water depth of 1.4 m and a flow rate of .32 lps the detention time is 4.4 hours.

The flow entering the clarifier is diverted downward by a baffle to discourage short-circuiting.

The effluent trough can be moved longitudinally along the water surface for maximum efficiency. The effluent trough is equipped with V-notches 2.54 cm deep.

The settled water flows from the collection trough through 2.54 cm diameter flexible Tygon tubing to a collection box on the side of the clarifier. The storage capacity of the collection box reduces fluctuations of the discharge through the filtration columns and gives entrapped air bubbles a chance to escape through the top.

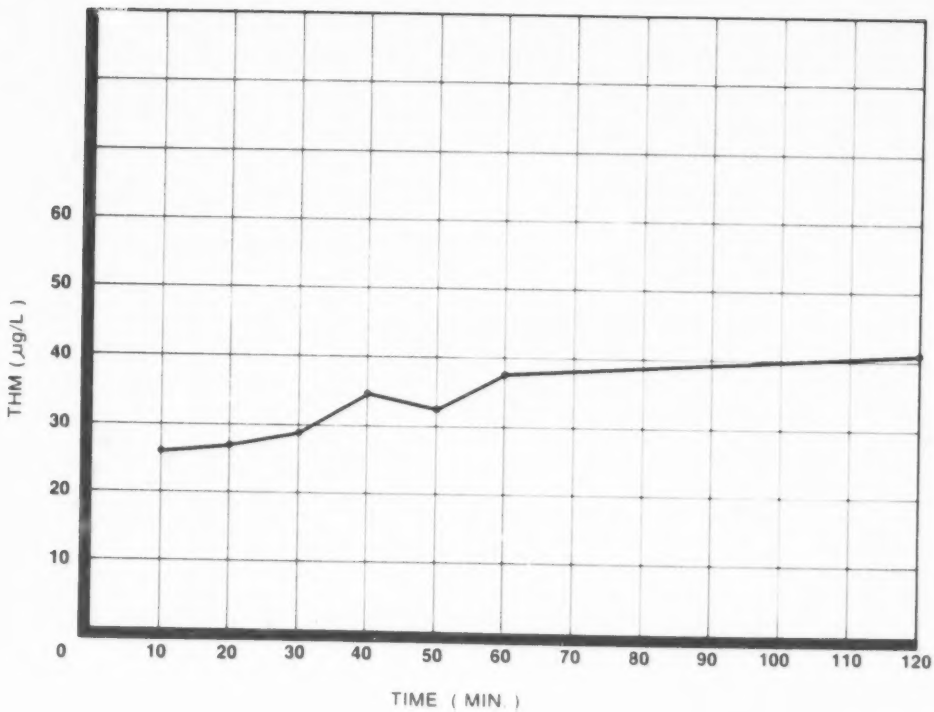
The settled water is pumped from the collection box to the filter columns. The filters are constructed of stainless steel. Each filter unit is .3 m by .2 m in cross-section and 1.8 m deep . The design flow rate for each unit is .16 lps. The filtration loading rate is 2.6 lps/sm. Design flow is obtained using two filter units in parallel. Glass ports are provided on the filters to observe the filter media.

The filtered water flows to the stainless steel clearwell measuring 1.8 m long by 1.5 m high by 0.3 m wide. Clearwell tank capacity is 530 L. A 15 cm by 15 cm opening in the top is provided for adding chemicals and for inspection. A mixer with three paddles is mounted in the center of the tank. It provides rapid mixing of disinfectants introduced into the tank.

The pilot plant was designed and constructed by faculty, staff, and students at the University of Missouri-Columbia, under a research project funded by the U. S. Environmental Protection Agency. It has continued to provide a valuable research tool on various research projects such as this. Additional information on this pilot plant can be obtained from the Municipal Environmental Research Center, U. S. Environmental Protection Agency, Cincinnati, Ohio.

APPENDIX E

TRIHALOMETHANE FORMATION CURVES



CHLORINE DOSE-15 mg/L

FIGURE E-1. PILOT PLANT EFFLUENT (TEST) THM FORMATION CURVE
AUGUST 19, 1983

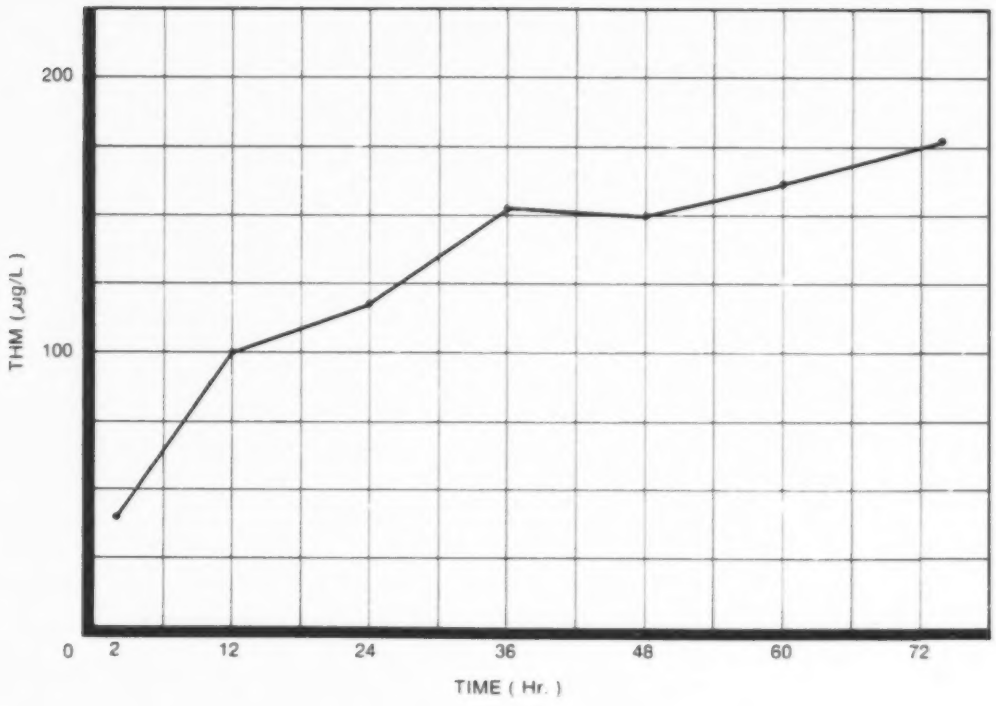
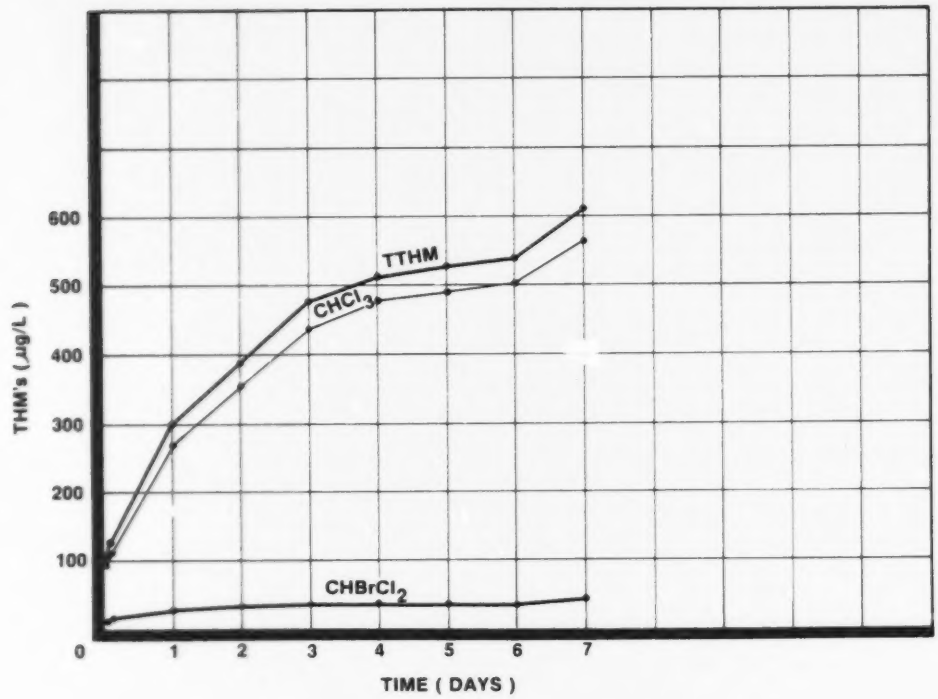
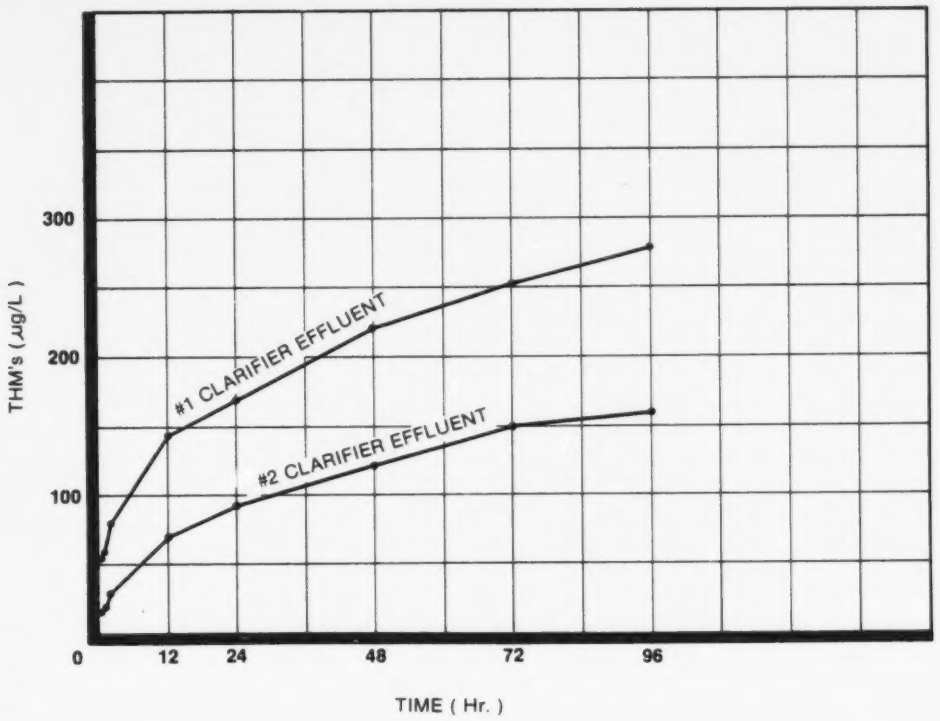


FIGURE E-2. PILOT PLANT EFFLUENT THM FORMATION CURVE
AUGUST 19, 1983



CHLORINE DOSE-35 mg/L

FIGURE E-3. BRENNAN PLANT RAW WATER THM FORMATION CURVE
NOVEMBER 2, 1983



#1 CLARIFIER: LIME - 220 mg/L
NALCO 8184 - 0.1 mg/L

#2 CLARIFIER: LIME - 220 mg/L
NALCO 8184 - 0.1 mg/L
FERRIC SULPHATE - 10 mg/L
XE-392 - 18 mg/L

CHLORINE DOSE-20 mg/L
pH-8.3

FIGURE E-4. BRENNAN PLANT CLARIFIER EFFLUENT THM FORMATION CURVE
OCTOBER 1, 1983

APPENDIX F

GC/MS AND TOX ANALYSES

GC/MS

Samples were collected for GC/MS analysis by USEPA during phase two of the project and again during phase three (plant scale trial). Pilot plant samples also were analyzed in the research laboratories of the Rohm and Haas Co. Of the samples analyzed, the plant scale samples showed fewer peaks and lower concentrations than those samples taken during the pilot plant run. Results indicated the presence of no unexpected compounds at concentrations greater than 1 µg/L which could be attributed to the XE-392 coagulant.

TOX

Samples were collected for total organic halogen analyses (TOX) and analyzed by the USEPA Municipal Environmental Research Laboratory in Cincinnati, during the plant scale trial. Raw water TOX values ranged from 14 to 112 µg/L for an average of 44 µg/L. Samples collected from the control clarifier contained an average 631 µg/L TOX. By comparison, samples taken from the test clarifier contained an average of 511 µg/L TOX, a 19% reduction.